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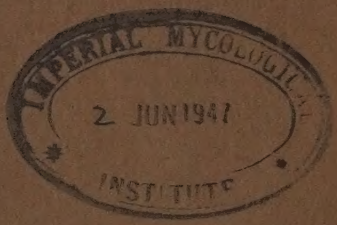


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*MATHEMATICS*

# ON THE «ANALOGY PROPERTY» OF DIRICHLET'S *L*-SERIES AND SIEGEL'S THEOREM ON $k(\sqrt{-D})$

By U. V. LINNIK

*(Communicated by I. M. Vinogradow, Member of the Academy, 24.XI.1942)*

The present note is concerned with some corollaries of a certain «analogy property» of Dirichlet's *L*-series. As I intend to publish some applications of this property to the evaluation of the number of classes $k(\sqrt{-D})$, I here outline the proof of Siegel's theorem on $h(-D)$ obtained by means of this property.

Although this method requires a considerably complicated analytical apparatus, it yields a new point of view on Siegel's theorem, as well as some new facts, which I hope to publish in the future.

Let $-D$ be a fundamental discriminant; $\left(\frac{-D}{n}\right)$, Kronecker's symbol; $\lambda(n)$, Liouville's symbol defined by the equality

$$\frac{\zeta(2s)}{\zeta(s)} = \sum_{n=1}^{\infty} \frac{\lambda(n)}{n^s} \quad (\sigma > 1).$$

Then, as it is easy to deduce from the elementary theory of $k(\sqrt{-D})$, *we shall have*

$$\left(\frac{-D}{n}\right) = \lambda(n)$$

*provided that no one of the prime factors of n is representable by quadratic forms* $Q(x, y)$ *of discriminant* $-D$. It is exactly in this remark that our «analogy property» is expressed.

Let $\chi_k(n)$ by any character $(\mathrm{mod}\, k)$ of the I, II or III kind. We shall have (1)

$$\left| \sum_{n=1}^{M} \chi_k(n) \left(\frac{-D}{n}\right) \right| < 100\, k^2 \sqrt{D} \ln D. \tag{1}$$

Let the series $L_k(s) = \sum_{n=1}^{\infty} \chi_k(n)\, n^{-s}$ $(\sigma > 1,\ k$ is fixed) have a zero $\rho = \beta + \gamma i$ with $\beta > \frac{1}{2}$.

Then it is evident that the series

$$\frac{L_k(2s)}{L_k(s)} = \sum_{n=1}^{\infty} \chi_k(n)\, \lambda(n)\, n^{-s} \quad (\sigma > 1)$$

cannot converge for $\sigma < \beta$, and thus we shall have for any $\varepsilon > 0$

$$\left| \sum_{n \leqslant M} \chi_k(n)\,\lambda(n) \right| = \Omega\left(M^{\beta-\varepsilon}\right). \tag{2}$$

A close comparison of (1) with (2) and the well known Hecke's lemma ([2]) give Siegel's theorem, but require a rather difficult analysis.

In what follows $k_1, k_2, \ldots$ will denote constants $> 2$.

$c_1, c_2, \ldots$ are constants.

Lemma. *Suppose that* $D_1 = D^{k_1}$ *and*

$$\left| \sum_{n \leqslant M_1} \chi_k(n)\,\lambda(n) \right| > D_1^{1-\eta}, \quad \eta < \frac{1}{4}. \tag{3}$$

*If* $D > a_1(k)$, *then*

$$h(-D) > D^{\frac{1}{2}-2k_1\eta}.$$

Putting

$$S_1 = \sum_{n \leqslant D_1} \chi_k(n) \left(\frac{-D}{n}\right), \quad S_2 = \sum_{n \leqslant D_1} \chi_k(n)\,\lambda(n),$$

we obtain

$$S_1 - S_2 = \sum a_j \sum_{n \leqslant \frac{D_1}{p_1 \ldots p_j}} \left(\frac{-D}{n}\right) \chi_h(n),$$

where $a_j = O\left(D_1^{\varepsilon}\right)$ and $p_1, p_2, \ldots p_j$ run through the primes representable by the forms $Q(x, y)$ of discriminant $-D$. If $\frac{D_1}{2^{n+1}} > \sqrt{D}$, the segment $\left[\frac{D_1}{2^{n+1}}, \frac{D_1}{2^k}\right]$ contains no more than $c_1 \frac{h}{\sqrt{D}} \cdot \frac{D_1}{2^k}$ of such $p$'s; if $h = h(-D) < D^{\frac{1}{2}-2k_1\eta}$, then there are less than $c_1 \frac{D_1^{1-2\eta}}{2^k}$ numbers $p$ on the segment $\left[\frac{D_1}{2^{n+1}}, \frac{D_1}{2^k}\right]$. Combining this estimation with (1) and (3), we obtain a contradiction.

Let the series

$$L_k(s) = \sum_{n=1}^{\infty} \chi_k(n)\, n^{-s}$$

have a zero $\rho = \beta + \gamma i$ with $\beta > 0.9$.

Then (2) holds, and to obtain Siegel's theorem it is sufficient to improve (2) as follows: for $D > a_2(k, \varepsilon)$ there exists $D_1$ between $D^{k_1}$ and $D^{k_2}$ such that

$$\left| \sum_{n \leqslant D_1} \chi_k(n)\,\lambda(n) \right| > D_1^{\beta-\varepsilon}. \tag{4}$$

For this purpose we may use Abel's method of summation of Dirichlet's series by means of Cohen-Mellin's integrals ([3]). From the formula

$$\int_0^{\infty} y^{s-1} e^{-y^m}\, dy = \frac{1}{m}\,\Gamma\left(\frac{s}{m}\right), \quad (m > 0,\ \sigma > 0)$$

by Mellin's inversion formula we obtain

$$e^{-x^m} = \frac{1}{2\pi i m} \int_{2-i\infty}^{2+i\infty} x^{-w}\,\Gamma\left(\frac{w}{m}\right) dw, \quad (x > 0).$$

For $0<\delta<\frac{1}{k}$, $\sigma>\frac{1}{2}$, $s-nm\neq\rho_k$ with integral $n$, where $\rho_k$ runs through the zeros of $L_k(s)$, we shall have [3]:

$$\sum_{nm<1}\delta^{nm}\frac{L_k(2(s-nm))}{L_k(s-nm)}=\sum_{n=1}^{\infty}\chi_k(n)\lambda(n)e^{-(\delta n)^m}n^{-s}-$$

$$-\frac{1}{m}\sum_{\rho_k}\operatorname{res}\left\{\delta^{s-w}\Gamma\left(\frac{w-s}{m}\right)\frac{L_k(2w)}{L_k(w)}\right\}+O(1)$$

where $O(1)$ is understood at $k\to\infty$ and the summands of the sum $\sum_{\rho_k}\operatorname{res}=$ $=\sum(\delta)$ are grouped in such a way that the zeros $\rho=\beta+\gamma i$ and $\rho'=\beta'+$ $+\gamma' i$ with $|\gamma-\gamma'|<\exp(-c_3\gamma/\ln\gamma)+\exp(-c_3\gamma'/\ln\gamma')$ belong to the same group.

Now put $s=\beta-\Delta$, where $2\varepsilon<\Delta<3\varepsilon$ and $s\neq\rho_k$. Choosing appropriate values for $m=\frac{1}{k_1}$ and $k_2$ and putting $D_2=D^{k_2}$ and $\delta_2=\frac{1}{D_2}$, we can show that $|\sum(\delta_2)|>D_2^{1,5\varepsilon}$, whence it is easy to deduce the existence of the required $D_1=D^{k_3}$, for which $\left|\sum_{n\leqslant D_1}\chi_k(n)\lambda(n)\right|>D_1^{\beta-\varepsilon}$.

The main difficulty, which one can overcome by using Vandermonde's determinants, is the investigation of the cases, when the distance between the roots is abnormally small.

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*MATHEMATICS*

# ON SEPARATION IN TOPOLOGICAL SPACES

By N. A. SHANIN

*(Communicated by A. N. Kolmogoroff, Member of the Academy, 1.VI.1942)*

In the present note we use the terminology and notations introduced in (1). In particular, if $\mathfrak{A}$ is a family of some subsets of the set $E$, $E\{\mathfrak{A}\}$ will denote the family of complements in $E$ of sets of the family $\mathfrak{A}$.

## § 1. Special Types of Families of Closed Sets

Let $E$ be a $T$-space and $\mathfrak{A} \subset \mathfrak{F}_E$; the family $\mathfrak{A}$ will be called normal if for any sets $F \in \mathfrak{A}$, $G \in E\{\mathfrak{A}\}$ with $F \subset G$ there exist such $F' \in \mathfrak{A}$ and $G' \in E\{\mathfrak{A}\}$ that $F \subset G' \subset F' \subset G$; we shall call the family $\mathfrak{A}$ weakly regular if, whatever be the set $F \in \mathfrak{A}$ and the point $x \in E - F$, there exists such $G \in E\{\mathfrak{A}\}$ that $F \subset G \subset E - (x)$; the family $\mathfrak{A}$ will be called regular if, whatever be the set $F \in \mathfrak{A}$ and the point $x \in E - F$, there exist $G \in E\{\mathfrak{A}\}$ and $F' \in \mathfrak{A}$ such that $F \subset G \subset F' \subset E - (x)$.

For the sake of brevity we shall say that the family $\mathfrak{Q}$ is conjugate to the family $\mathfrak{P}$ if for any two sets $P \in \mathfrak{P}$ and $Q \in \mathfrak{Q}$ with $P \subset Q$ there exist sets $P' \in \mathfrak{P}$ and $Q' \in \mathfrak{Q}$ such that $P \subset Q' \subset P' \subset Q$. Suppose that $E$ is a $T$-space and $\mathfrak{A} \subset \mathfrak{F}_E$; the pair of sets $\{F, G\}$ will be called canonical with respect to the family $\mathfrak{A}$ if $F \subset G$ and there exist such families $\mathfrak{P}$ and $\mathfrak{Q}$ that $F \in \mathfrak{P} \subset \mathfrak{A}$, $G \in \mathfrak{Q} \subset E\{\mathfrak{A}\}$ and $\mathfrak{Q}$ is conjugate to $\mathfrak{P}$. The family $\mathfrak{A} \subset \mathfrak{F}_E$ will be called completely regular if for any $F \in \mathfrak{A}$ and $x \in E - F$ there exists a set $G \in E\{\mathfrak{A}\}$ such that $F \subset G \subset E - (x)$ and the pair of sets $\{F, G\}$ is canonical with respect to the family $\mathfrak{A}$.

A $T$-space $E$ will be called respectively normal, weakly regular, regular or completely regular according as $\mathfrak{F}_E$ is a normal, weakly regular, regular or completely regular family *. As to the definitions of $T_0$-, $T_1$- and $T_2$-spaces, we refer the reader to the book by P. Alexandroff and H. Hopf. It is evident that every $T_1$-space is weakly regular and every weakly regular normal family is completely regular.

## § 2. Separation in $(\omega, \mathfrak{B})$-Extensions of $T$-Spaces

Theorem 1. *Let $R$ be a $T$-space. Suppose that $\mathfrak{B}$ is a reduced closed basis of $R$ and $S$ is the $(\omega, \mathfrak{B})$-extension of $R$. In order that $S$ be respectively:* a) *a normal $T$-space*, b) *a weakly regular $T$-space*, c) *a regular $T$-space*, d) *a completely regular $T$-space*, e) *a $T_0$-space*, f) *a $T_1$-space*, g) *a $T_2$-space, it is*

* The difference between our definitions and the usual ones is that neither $T_1$- nor $T_0$-axiom is supposed to be fulfilled.

*necessary and sufficient that respectively:* a) $\Delta\mathfrak{B}$ *be a normal family,* b) $\Delta\mathfrak{B}$ *be a weakly regular family,* c) $\Delta\mathfrak{B}$ *be a regular normal family,* d) $\Delta\mathfrak{B}$ *be a completely regular normal family*,* e) $R$ *be a* $T_0$*-space,* f) $R$ *be a* $T_1$*-space and* $\Delta\mathfrak{B}$ *be a weakly regular family,* g) $R$ *be a* $T_2$*-space and* $\Delta\mathfrak{B}$ *be a weakly regular normal family.*

The theorem follows from a series of lemmas.

Lemma 1. *Let* $\mathfrak{A}$ *be a closed basis of a bicompact* $T$*-space* $E$*. If* $F_1 \in \mathfrak{F}_E$, $F_2 \in \mathfrak{F}_E$ *and* $F_1 \cdot F_2 = \Lambda$*, then there exist such* $P_1 \in \Delta\mathfrak{A}$ *and* $P_2 \in \Delta\mathfrak{A}$ *that* $F_1 \subset P_1$, $F_2 \subset P_2$ *and* $P_1 \cdot P_2 = \Lambda$*. If* $F \in \mathfrak{F}_E$, $G \in \mathfrak{G}_E$ *and* $F \subset G$*, then there exist* $P \in \Delta\mathfrak{A}$ *and* $H \in E\{\Delta\mathfrak{A}\}$ *such that* $F \subset P \subset H \subset G$.

Lemma 2. *Let* $\mathfrak{A}$ *be a closed basis of a bicompact* $T$*-space* $E$*. In order that* $E$ *be respectively:* a) *normal,* b) *weakly regular,* c) *regular,* d) *completely regular, it is necessary and sufficient that the family* $\Delta\mathfrak{A}$ *be respectively:* a) *normal,* b) *weakly regular,* c) *regular,* d) *completely regular.*

Lemma 3. *If* $\mathfrak{A}$ *is a closed basis of a bicompact regular* $T$*-space (in particular, of a bicompact* $T_2$*-space), then* $\Delta\mathfrak{A}$ *is a completely regular normal family.*

Lemma 4. *Let* $R$ *be a subspace of a* $T$*-space* $S$ *and* $\mathfrak{B} \subset \mathfrak{F}_R$*. If* $\mathfrak{B}$ *is* $\Pi$*-separated in* $S$, $F \in \Delta\mathfrak{B}$, $G \in R\{\Delta\mathfrak{B}\}$ *and* $F \subset G$*, then* $\overline{F}^S \subset \eta_S(G)$.

Lemma 5. *Let* $R$ *be a subspace of a* $T$*-space* $S$, $\mathfrak{E} \subset \mathfrak{F}_S$ *and let* $\mathfrak{B}$ *denote the family of sets of the form* $P \cdot R$*, where* $P \in \mathfrak{E}$*. If the family* $\mathfrak{E}$ *is respectively:* a) *weakly regular,* b) *regular,* c) *completely regular, then the family* $\mathfrak{B}$ *is also respectively:* a) *weakly regular,* b) *regular,* c) *completely regular. If* $\mathfrak{E}$ *is a normal family,* $\mathfrak{B}$ *is* $\Pi$*-separated in* $S$ *and* $\mathfrak{E} = \{\overline{F}^S\}_{F \in \mathfrak{B}}$*, then* $\mathfrak{B}$ *is also a normal family.*

Lemma 6. *If* $R$ *is a subspace of a* $T$*-space* $S$, $\overline{R}^S = S$ *and* $F \in \mathfrak{F}_R$*, then* $\eta_S(F_R) \subset \overline{F}^S$.

Lemmas 2, 3 and 5 are to be used in the proof of the necessity in Theorem 1; Lemmas 1 (the second part), 2, 4 and 6—in the proof of the sufficiency.

## § 3. Weight-Preserving Bicompact Extensions of $T$-Spaces

By the weight of a $T$-space is meant the minimum of powers of closed bases in the space.

Theorem 2. *Every normal* $T$*-space can be extended to a bicompact normal* $T$*-space so that the weight rests invariant**.*

We first note that every infinite closed basis $\mathfrak{A}$ of a normal $T$-space $R$ can be complemented to a reduced closed basis $\mathfrak{B}$ by a process consisting of enumerably many steps and leaving invariant the power of the basis in such a way that $\mathfrak{B}$ is a normal family and $\Delta\mathfrak{B} = \mathfrak{B}$. If $\mathfrak{A}$ is chosen under the condition that the power of $\mathfrak{A}$ is equal to the weight of $R$, then by Theorem 1 the $(\omega, \mathfrak{B})$-extension of $R$ is the required extension.

Theorem 1 and Lemmas 2 and 5 imply

Theorem 3. *The weakly regular* $T$*-space* $R$ *(resp.* $T_1$*-space* $R$*) of infinite weight can be extended to a bicompact weakly regular* $T$*-space (resp. a bicompact* $T_1$*-space) of the same weight if and only if the weight of* $R$ *is the minimum of powers of exactly those closed bases in* $R$ *that form weakly regular families.*

As is easily seen, every infinite closed basis of a regular $T$-space can be complemented to a closed basis of the same power that forms a weakly regular family. Thus, every regular $T$-space (resp. every regular $T_1$-space) can be extended to a bicompact weakly regular $T$-space (resp. a bicompact $T_1$-space). On the other hand, there exist $T_2$-spaces even of enumerable weight that can-

* Conditions c) and d) are, obviously, equivalent.

** For normal $T_1$-spaces this theorem was proved by A. Tychonoff (3).

not be extended to bicompact weakly regular $T$-spaces of the same weight*. We passingly note that according to Theorem 1 every $T_0$-space can be extended to a bicompact $T_0$-space of the same weight.

Theorem 4. *Every completely regular $T$-space can be extended to a bicompact completely regular $T$-space in a weight-preserving manner* **.

To prove Theorem 4 we introduce some notions and state some theorems that are important also in other cases.

A closed set $F$ in a $T$-space $E$ is called completely closed if $F$ is the set of zeros of a continuous function on $E$ [following Vedenissof ([3]), it is easy to prove that the closed set $F$ in a $T$-space $E$ is completely closed if and only if there exist finite or enumerable families $\mathfrak{P}$ and $\mathfrak{Q}$ such that $\mathfrak{P} \subset \mathfrak{F}_E$, $\mathfrak{Q} \subset \mathfrak{G}_E$, $\mathfrak{Q}$ is conjugate to $\mathfrak{P}$ and $\prod_{Q \in \mathfrak{Q}} Q = F \in \mathfrak{P}$]. The family of all completely closed sets in the $T$-space $E$ will be denoted by $\mathfrak{F}_E^+$. As is easily seen, if the famity $\mathfrak{F}_E^+$ is a closed basis of the $T$-space $E$, then the latter is completely regular. Conversely, if $E$ is a completely regular $T$-space, then, as it was established by A. Alexandroff ([4]), $\mathfrak{F}_E^+$ is a reduced closed basis of $E$ that forms a weakly regular normal (consequently, a completely regular) family*** with the property: the intersection of a finite or enumerable number of elements of $\mathfrak{F}_E^+$ is an element of $\mathfrak{F}_E^+$.

Lemma 7. *Every completely regular $T$-space $R$ of infinite weight contains a reduced closed basis $\mathfrak{B}$, the power of which is equal to the weight of $R$ and which forms a completely regular normal family and possesses the property*: $\Delta\mathfrak{B} = \mathfrak{B}$.

This lemma can be established as follows: we choose from $\mathfrak{F}_R^+$ a closed basis of the $T$-space $R$ that forms a weakly regular family and is of a power equal to the weight of $R$; we complement it (by induction) by elements of $\mathfrak{F}_R^+$ so as to obtain a normal family $\mathfrak{B}$ such that the sum and the intersection of any finite number of elements of $\mathfrak{B}$ also belong to $\mathfrak{B}$.

If $\mathfrak{B}$ denotes the closed basis of $R$ mentioned in Lemma 7, then the $(\omega, \mathfrak{B})$-extension of $R$ is a bicompact completely regular extension of $R$ of the same weight as $R$. Theorem 4 is thus proved. If $R$ is a completely regular $T_1$-space, then the $(\omega, \mathfrak{B})$-extension just constructed is also a $T_1$-space.

## § 4. Separation in $(\chi, \mathfrak{B})$-Extensions of $T$-Spaces

Theorem 5. *The $(\chi, \mathfrak{B})$-extension of a $T$-space $R_{\mathfrak{B}}^{\chi}$ is a $T_0$-space if and only if $R$ is a $T_0$-space itself.*

Theorem 6. *The $(\chi, \mathfrak{B})$-extension of the $T$-space $R$ is weakly regular if and only if the following condition is fulfilled: if $F \in \Delta\mathfrak{B}$ and $x \in R - F$, there exist $G \in R\{\Delta\mathfrak{B}\}$ and $H \in \mathfrak{G}_R$ such that $F_R \subset \overline{G}^R$, $G \subset H$ and $F \subset H \subset R - (x)$.*

Theorem 7. *In order that the $(\chi, \mathfrak{B})$-extension of $T$-space $R$ be a $T_1$-space, it is necessary and sufficient that the following conditions be fulfilled:* 1) *$R$ is a $T_1$-space,* 2) *if $F \in \Delta\mathfrak{B}$ and $x \in R - F$, there exists such $G \in R\{\Delta\mathfrak{B}\}$ that $F_R \subset \overline{G}$ and $G \subset R - (x)$.*

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* Consider an example: $E^2$ is the coordinate plane, $P$ is the closed upper semi-plane, $E$ is the axis of abscissae, $R$ is the set of rational points of $E$. The following sets will be considered as closed in $P$: 1) natural closed subsets of $P$ and 2) sets of the form $F+(P-E)+R$, where $F$ is of the first kind. $P$ thus becomes a $T_2$-space of enumerabfe weight. But every closed basis of $P$ that forms a weakly regular family is non-enumerable. The proof of this fact is based on the following well known theorem: the set of all irrational points lying in a non-empty natural open subset $G$ of the real axis cannot be represented as the sum of a finite or enumerable number of natural closed subsets of the real axis.

** For completely regular $T_1$-spaces this theorem was proved by A. Tychonoff ([2]).

*** Completely regular $T$-spaces may be characterized by the following property: they contain such closed bases that form weakly regular normal families.

A closed basis $\mathfrak{B}$ of a $T$-space $R$ will be called symmetric if: 1) $\Lambda \in \mathfrak{B}$, 2) the sum and the intersection of any finite number of elements of $\mathfrak{B}$ belong to $\mathfrak{B}$, 3) if $\mathfrak{B}$ contains the set $F$, then $R - F_R$ also belongs to $\mathfrak{B}$.

Theorem 8. *If $\mathfrak{B}$ is a symmetric basis of a $T_2$-space $R$, then the $(\chi, \mathfrak{B})$-extension of $R$ is also a $T_2$-space.*

Theorem 9. *Every weakly regular $T$-space (resp. every $T_1$-space, every $T_2$-space) $R$ can be extended to a quasi-bicompact weakly regular $T$-space (resp. to a quasi-bicompact $T_1$-space, to an $H$-closed $T_2$-space)* of the same weight. Moreover, it may be carried out so that the family of closed sets in $R$ becomes a closed framework of the extension.*

The proof of Theorem 9 is based on the following facts: 1) the symmetric closed basis of a $T$-space satisfies the conditions of Theorems 6 and 7, 2) every infinite closed basis of a $T$-space can be complemented to a symmetric closed basis of the same power.

Theorem 10. *In order that the $(\chi, \mathfrak{B})$-extension of a $T$-space $R$ be regular (completely regular), it is necessary and sufficient that the following conditions be fulfilled:* 1) *if $F \in \Delta\mathfrak{B}$ and $\overline{F}_R = \Lambda$, then $F$ is a bicompact subset of $R$,* 2) *the family $\Delta\mathfrak{B}$ is regular and normal.*

The theorem follows from the fact that the quasi-bicompact regular (completely regular) $T$-space is bicompact and the bicompact $(\chi, \mathfrak{B})$-extension of $R$ is the $(\omega, \mathfrak{B})$-extension of $R$.

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* The last assertion was first proved by M. H. Stone ([5]).

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*ASTRONOMY*

# PHOTOMETRIC INVESTIGATION OF THE SYSTEM OF U SAGITTAE

By N. I. TCHUDOVITCHEV

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1. The fluctuations of brightness in U Sagittae were discovered by F. Schwab in 1901 (1). By the character of its light the star is the most bright and typical representative of algols, having a period of variability of $3^m.38$, a primary minimum of a large amplitude of about $3^m$, and a secondary minimum of a very small depth, less than $0^m.1$.

Ever since its discovery it has been intensively studied both by the method of estimates and photometrically, but nearly all of these observations centered about the primary minimum. The number of observations made in the maximum of brightness is quite insufficient, and no reliable calculation of the orbit can be done on the basis of the available data, because one is denied the possibility of making allowance for the subtle effects (elliptical, reflection, etc.) that can only be determined from the brightness of the star outside the eclipses.

Of the series of reported observations only those carried out by K. Walter permit to trace the light-curve in the maximum with sufficient certitude. By taking photographs of the star in two rays, Walter obtained in red rays a marked effect of ellipticity of its components which is scarcely noticeable on the photographic light-curve. He put forward the assumption that the large red component is strongly elliptical. In fact, spherical compounds may hardly be supposed to form so close a pair as that of U Sagittae. Nevertheless, it is just on the basis of such supposition that the photometric elements of the system have been computed by Russel, Fowler, Borton (2) and Fetlaar (3).

From 1907 onwards U Sagittae has also been studied spectroscopically by many observers. The spectroscopical elements of its orbit have been obtained by Fowler (4) and Joy (5). However, there is strong discrepancy between the estimates of the longitude of its periastrum, as made by differents observers.

So our knowledge of the system of U Sagittae has up to the present remained in a rather unsettled state. That is the reason why the study of this interesting variable has made an item in the working programme of the Engelhardt observatory.

2. The observations of U Sagittae were carried on from August 1937 till September 1940 in two rays by means of the Heyde astrograph with a Zeiss lens of the Astro-Triplet type. The method of multiple exposures being used, there was obtained 1508 exposures in all. Of them 696 in photographic rays on the Ilford Monarch plates, and 812 in photovisual rays on Soft-Gradation Panchromatic plates with a Schott's filter GG-11. Photographically active was found to be the region confined within $\lambda = 5000-6500$ Å, which indicated a greater sensitivity to red rays than that of the eye.

In subjecting the plates to photometric measurement, use was made of B. Nikonov's photoelectric microphotometer made at the Astronomical Institute of Leningrad.

The method adopted in carrying out the measurements and in treating the results obtained has been described by me in an earlier paper (6).

The magnitudes of the comparison stars were determined with reference to the *NPS*. Their ultimate brightnesses as well as colour-indices and spectra are given in Table 1.

Table 1

| *BD* | Spectrum | Brightness | | Colour-index |
|---|---|---|---|---|
| | | Photo-graphic | Photo-visual | |
| 19°4000 | A0 | $6^m.22$ | $6^m.30$ | $-0^m.08$ |
| 19 3956 | — | 6 .90 | 5 .76 | +1 .14 |
| 18 4043 | F5 | 7 .17 | 6 .62 | +0 .55 |
| 18 4014 | — | 7 .45 | 6 .85 | +0 .60 |
| 19 3976 | A0 | 7 .95 | 7 .98 | −0 .03 |
| 19 3978 | A2 | 8 .57 | 8 .40 | +0 .17 |
| 19 3981 | K0 | 9 .27 | 8 .11 | +1 .16 |
| 19 3987 | — | 9 .75 | 9 .29 | +0 .46 |
| 19 3974 | — | 10 .47 | 9 .44 | +1 .03 |

All the observations of U Sagittae are gathered to normal points listed in Tables 2 and 3. In the last column is given the number of ponderable individual observations referring to the respective normal point. The normal points of the primary minimum comprise a smaller number of observations, and so they weigh less compared to the rest. But as they are more densely situated, it may be taken for granted that all parts of the light-curve have nearly equal weight.

Table 2

Normal Points on Photovisual Light-Curve of U Sagittae

| Nos. of points | Phases | *m* | *n* | Nos. of points | Phases | *m* | *n* |
|---|---|---|---|---|---|---|---|
| 1 | 0.026 | 9.00 | 5 | 33 | 1.628 | 6.44 | 13 |
| 2 | 0.043 | 8.95 | 5 | 34 | 1.660 | 6.46 | 14 |
| 3 | 0.060 | 8.68 | 5 | 35 | 1.695 | 6.48 | 16 |
| 4 | 0.074 | 8.27 | 5 | 36 | 1.753 | 6.46 | 15 |
| 5 | 0.091 | 7.87 | 5 | 37 | 1.836 | 6.41 | 17 |
| 6 | 0.099 | 7.78 | 8 | 38 | 1.884 | 6.38 | 17 |
| 7 | 0.128 | 7.36 | 10 | 39 | 1.933 | 6.40 | 17 |
| 8 | 0.154 | 7.02 | 9 | 40 | 2.012 | 6.35 | 15 |
| 9 | 0.170 | 6.88 | 11 | 41 | 2.113 | 6.34 | 15 |
| 10 | 0.189 | 6.77 | 11 | 42 | 2.159 | 6.35 | 15 |
| 11 | 0.218 | 6.65 | 11 | 43 | 2.205 | 6.35 | 15 |
| 12 | 0.261 | 6.48 | 12 | 44 | 2.286 | 6.38 | 15 |
| 13 | 0.337 | 6.39 | 15 | 45 | 2.434 | 6.34 | 14 |
| 14 | 0.400 | 6.36 | 16 | 46 | 2.510 | 6.36 | 14 |
| 15 | 0.440 | 6.37 | 15 | 47 | 2.548 | 6.37 | 15 |
| 16 | 0.481 | 6.37 | 16 | 48 | 2.594 | 6.36 | 15 |
| 17 | 0.526 | 6.36 | 14 | 49 | 2.604 | 6.34 | 15 |
| 18 | 0.614 | 6.41 | 15 | 50 | 2.762 | 6.35 | 14 |
| 19 | 0.731 | 6.36 | 15 | 51 | 2.805 | 6.34 | 14 |
| 20 | 0.791 | 6.35 | 15 | 52 | 2.855 | 6.35 | 14 |
| 21 | 0.832 | 6.35 | 15 | 53 | 2.925 | 6.38 | 15 |
| 22 | 0.876 | 6.35 | 15 | 54 | 3.037 | 6.40 | 15 |
| 23 | 0.943 | 6.36 | 14 | 55 | 3.086 | 6.41 | 15 |
| 24 | 1.048 | 6.34 | 15 | 56 | 3.150 | 6.50 | 15 |
| 25 | 1.111 | 6.34 | 15 | 57 | 3.192 | 6.69 | 14 |
| 26 | 1.144 | 6.34 | 17 | 58 | 3.232 | 6.89 | 11 |
| 27 | 1.234 | 6.40 | 18 | 59 | 3.266 | 7.12 | 10 |
| 28 | 1.335 | 6.345 | 18 | 60 | 3.293 | 7.345 | 6 |
| 29 | 1.415 | 6.35 | 15 | 61 | 3.324 | 8.07 | 3 |
| 30 | 1.467 | 6.37 | 15 | 62 | 3.349 | 8.82 | 4 |
| 31 | 1.522 | 6.37 | 14 | 63 | 3.369 | 9.04 | 4 |
| 32 | 1.586 | 6.39 | 13 | 64 | 0.002 | 8.99 | 2 |

The mean quadratic error of one normal position in the maximum of brightness is of an order of $\pm 0^m.022$ in photographic rays; $\pm 0^m.011$ in photovisual rays. So the photovisual is the more accurate curve and as such has been placed at the basis of further computations.

Table 3

Normal Points on Photographic Light-Curve of U Sagittae

| Nos. of points | Phases | $m$ | $n$ | Nos. of points | Phases | $m$ | $n$ |
|---|---|---|---|---|---|---|---|
| 1 | 0.011 | 9.70 | 8 | 28 | 1.533 | 6.44 | 17 |
| 2 | 0.029 | 9.73 | 7 | 29 | 1.599 | 6.47 | 16 |
| 3 | 0.045 | 9.68 | 8 | 30 | 1.664 | 6.44 | 19 |
| 4 | 0.058 | 9.13 | 9 | 31 | 1.723 | 6.41 | 20 |
| 5 | 0.078 | 8.46 | 11 | 32 | 1.789 | 6.43 | 20 |
| 6 | 0.089 | 8.11 | 10 | 33 | 1.863 | 6.45 | 18 |
| 7 | 0.107 | 7.685 | 9 | 34 | 1.929 | 6.38 | 16 |
| 8 | 0.125 | 7.46 | 10 | 35 | 2.020 | 6.41 | 12 |
| 9 | 0.155 | 7.055 | 10 | 36 | 2.136 | 6.38 | 17 |
| 10 | 0.169 | 6.955 | 10 | 37 | 2.198 | 6.35 | 17 |
| 11 | 0.196 | 6.85 | 10 | 38 | 2.280 | 6.405 | 15 |
| 12 | 0.235 | 6.55 | 10 | 39 | 2.429 | 6.435 | 16 |
| 13 | 0.279 | 6.44 | 10 | 40 | 2.530 | 6.415 | 17 |
| 14 | 0.369 | 6.42 | 12 | 41 | 2.595 | 6.37 | 17 |
| 15 | 0.431 | 6.40 | 16 | 42 | 2.720 | 6.37 | 17 |
| 16 | 0.486 | 6.395 | 16 | 43 | 2.823 | 6.40 | 20 |
| 17 | 0.560 | 6.44 | 14 | 44 | 2.942 | 6.43 | 18 |
| 18 | 0.688 | 6.41 | 14 | 45 | 3.088 | 6.40 | 16 |
| 19 | 0.766 | 6.37 | 18 | 46 | 3.158 | 6.58 | 10 |
| 20 | 0.818 | 6.385 | 14 | 47 | 3.185 | 6 67 | 10 |
| 21 | 0.944 | 6.38 | 13 | 48 | 3.216 | 6.92 | 10 |
| 22 | 1.056 | 6.37 | 15 | 49 | 3.237 | 7.01 | 8 |
| 23 | 1.115 | 6.34 | 21 | 50 | 3.267 | 7.36 | 8 |
| 24 | 1.157 | 6.365 | 22 | 51 | 3.287 | 7.64 | 9 |
| 25 | 1.219 | 6.39 | 22 | 52 | 3.328 | 8.51 | 5 |
| 26 | 1.400 | 6.40 | 13 | 53 | 3.349 | 9.40 | 6 |
| 27 | 1.467 | 6.37 | 15 | 54 | 3.370 | 9.65 | 9 |

Both curves show an asymmetric primary minimum; the descending branch has a more gentle slope than the ascending. In the maximum of brightness elliptical and reflection effects are noticeable. The former is more distinctly expressed on the photovisual curve. The depth of the primary and secondary minima is $2^m.68$ and $0^m.10$, respectively, in the photovisual rays; $3^m.34$ and $0^m.07$ in photographic rays. On both curves the duration of the constant brightness in the minimum is about $1^h.35^m$.

From the observed minima the normal minimum was derived:

| Date | O—C | |
|---|---|---|
| 2429216.1197 ± 8 | —0.0021 | photovisual |
| 2429216.1210 ± 6 | —0.0008 | photographic |

The deviations O—C are referred to Jacchia's elements [7], which for the present are the most accurate.

3. The calculation of orbits in the case of systems whose components are neither similar nor similarly situated is in point of theory a matter of great difficulty, and no reliable method of doing this has yet been reported in literature.

However, in 1941 a new method for calculating the elements of an orbit from asymmetric light-curve was worked out by A. Gainullin, of the Engelhardt Observatory. This method I used in the present case and found it on the main to be quite satisfactory. The final results of the calculation are reported to in Table 4.

Table 4

Photometric Elements of the U Sagittae (Hypothesis U)

| | | Light-curve | |
|---|---|---|---|
| | | Photovisual | Photographic |
| Inclination of orbit | $i$ | 90 | |
| Eccentricity of orbit | $e$ | 0.00* | |
| Ratio of semi-major axis | $k$ | 0.69 | |
| Ratio of semi-minor axis | $k_1$ | 0.80 | |
| Semi-major axis of the larger star | $a_1$ | 0.348 | |
| Semi-minor axis of the larger star | $b_1$ | 0.291 | |
| Semi-major axis of the smaller star | $a_2$ | 0.239 | |
| Semi-minor axis of the smaller star | $b_2$ | 0.233 | |
| Squared eccentricity of meridional section for the larger star | $\varepsilon_1^2$ | 0.30 | |
| Squared eccentricity of meridional section for the smaller star | $\varepsilon_2^2$ | 0.05 | |
| Pointing of major axis of the larger star | $\lambda_1$ | −15 | |
| Pointing of major axis of the smaller star | $\lambda_2$ | +25 | |
| Brightness of the larger star (at $\theta=105°$) | $L_1$ | 0.114 | 0.071 |
| Brightness of the smaller star (at $\theta=65°$) | $L_2$ | 0.886 | 0.929 |
| Constant of reflection (coefficient at $\cos\theta$) | $b$ | 0.014 | 0.015 |
| Ratio of surface intensities | $\frac{I_1}{I_2}$ | 0.071 | 0.042 |

* From the variation of the brightness range the eccentricity of orbit may be supposed to have an order of 0.005.

The geometric elements of the U Sagittae given in this table were obtained from the photovisual light-curve. On their basis theoretical light-curves were plotted and came out to agree well not merely with the photovisual, but also with photographic observations, which may be regarded as a verification of the obtained elements.

4. Making use of the spectroscopic elements secured by Joy ([5])

$$a\sin i = 3155\,000 \text{ km}, \quad \frac{m_2}{m_1} = 3.3$$

and of the data of Table 4, there were computed the absolute dimensions and a series of physical characteristics of the components of U Sagittae. The results of these computations are presented in Table 5.

Table 5

Absolute Characteristics of the Components of U Sagittae

| | | |
|---|---|---|
| Radius of orbit, the larger star | 10 410 000 km | 0.070 astronomical units |
| » » » the smaller star | 3 155 000 » | 0.021 » » |
| Radius of relative orbit | 13 565 000 » | 0.091 » » |
| Semi-major axis of the larger star | 4 721 000 » | 6.79 ⊙ |
| Semi-minor axis of the larger star | 3 947 000 » | 5.68 ⊙ |
| Semi-major axis of the smaller star | 3 242 000 » | 4.67 ⊙ |
| Semi-minor axis of the smaller star | 3 161 000 » | 4.55 ⊙ |
| Total mass of the components | | 8.8 ⊙ |
| Mass of the larger star | | 2.0 ⊙ |
| Mass of the smaller star | | 6.8 ⊙ |
| Volume of the larger star | | 21900 ⊙ |
| Volume of the smaller star | | 9670 ⊙ |
| Density of the larger star | | 0.009 ⊙ |
| Density of the smaller star | | 0.070 ⊙ |
| Spectrum of the larger star* | | gG2 |
| Spectrum of the smaller star* | | B9n |
| Absolute magnitude of the larger star in photovisual rays | | $+1^m.68$ |
| Do, in photographic rays | | +2 .43 |
| Absolute magnitude of the smaller star in photovisual rays | | −0.93 |
| Do, in photographic rays | | −0.97 |
| Parallax | | $0''.0034$ |

* According to Joy ([5]).

In determining the absolute magnitude of the star I used the well known relations:

$$M_v = \frac{29\,500}{T} - 5 \lg R - 0.08$$

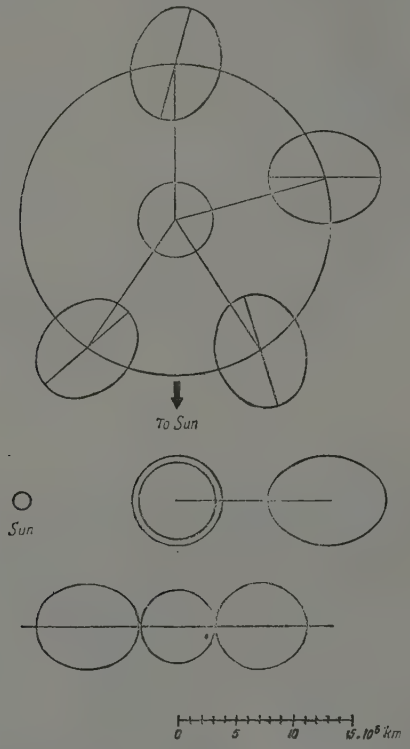
in the case of visual rays, and

$$M_p = \frac{36\,700}{T} - 5 \lg R - 0.72$$

in the case of photographic rays. For the radius I took the average value of the half-axis

$$R = \frac{a+b+c}{3}; \qquad b = c.$$

This gives 6.05 and 4.59 for the faint and the bright component, respectively, or, in logarithms, 0.782 and 0.662. The value of $T$ was put at 5200° for the lar-




Schematic representation of the system of U Sagittae. The upper half represents the position of the components in the orbit plane. The larger star is shown in four positions: 1) at the time of the first contact, 2) at the time of the fourth contact, 3) at one of the points corresponding to maximum brightness, and 4) in the middle of the secondary minimum. Below the same positions are given in the plane of the image. At the time of the first contact the visible disk of the large component is markedly elliptical ($\varepsilon_1 = 0.45$), while it is all but a circle ($\varepsilon_1 = 0.25$) at the fourth contact.

ger star, and at 12000° for the smaller star. The parallax was computed by means of the relation

$$M = m + 5 + 5 \lg \pi,$$

the absolute stellar magnitude being given.

Thus, in the system of U Sagittae, like in that of U Cephei, the smaller bright star is of nearly spherical shape, while the larger star is strongly elliptica (see figure).

5. From the data of Table 5 one may conclude that the larger star is a subgiant. Its absolute brightness and dimensions are by far less than in the typical stars of the same subdivision of the spectrum, and its density is higher. But the bright component is a normal star, its absolute brightness, size and density are near to the average values characterizing the ordinary stars of a similar spectrum.

In the future the attention of the observers should be directed towards securing an accurate photometric light-curve, if possible with the use of a photocell, sensitive to a far red region of the spectrum. By means of this curve the asymmetry of the primary minimum and the position of the secondary one can be ascertained with more precision. The importance of observations of radial velocities is too obvious to need special mentioning.

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*PHYSICS*

# NEW EXPERIMENTAL DATA ON THE STRUCTURE OF THE RAYLEIGH LINE IN BENZENE

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Recently we described a new method of investigating the distribution of intensity within the Rayleigh line (1), based on measuring the absorption of scattered light while the latter is passing through a resonance filter.

Now we shall give the experimental data for benzene and also the calculation of the shape of the line according to these data. Our exciting lines were *D*-natrium lines obtained from the State Optical Institute lamp. The scattered light passed through an absorption tube filled with natrium, 43.5 cm in length. In order to increase the absorption, nitrogen was introduced into the tube; the pressure of the nitrogen was measured with the aid of a manometer connected with the tube. At a temperature of 20° C the pressure was equal to 200 mm. The value of the transmittance $A$ was measured at different temperatures $T$ of the absorption tube.

For the case of a single resonance line the transmittance

$$A(T) = \frac{\int_{-\infty}^{+\infty} I(\Delta\nu)\, e^{-\frac{4\pi n x}{\lambda} l}\, d\nu}{\int_{-\infty}^{+\infty} I(\Delta\nu)\, d\nu} \tag{1}$$

where $I(\Delta\nu)$ is the distribution function of the intensity of the investigated line; $\Delta\nu = \nu_0 - \nu$, the distance from the centre of the line; $\lambda$, the wave-length of the middle of the line; $l$, the length of the absorbing layer; $nx$, the function of dispersion

$$nx = \frac{\rho}{64\pi^3\nu} \cdot \frac{\gamma}{\Delta\nu^2 + \left(\frac{\gamma}{4\pi}\right)^2} \tag{2}$$

where $\rho = 4\pi Nf \frac{e}{m}$. Here $e$ is the charge and $m$ the mass of an electron; $\gamma$, the damping constant; $Nf$, the number of scattering electrons per cm³. We can have for the exponent in equation (1)

$$\frac{4\pi n x l}{\lambda} = \frac{M}{\Delta\nu^2 + \left(\frac{\gamma}{4\pi}\right)^2}. \tag{3}$$

$M$ stands for

$$M = \frac{\rho\gamma l}{16\pi^3 c}; \tag{4}$$

$c$ is the velocity of light.

After the curve of the dependence of $A$ upon $T$ is plotted, the problem is reduced to the computation of the curve, showing the distribution of intensity of the line, i. e. to the finding of the function $I(\Delta\nu)$ from the integral equation (1).

In the present note we shall consider one way of solving this problem. Let us take the solution of the equation (1) in the following form:

$$I(\Delta\nu) = c_0\left(1 - e^{-\frac{k_0}{\Delta\nu^2}}\right) + c_1\left(1 - e^{-\frac{k_1}{\Delta\nu^2}}\right) + c_2\left(1 - e^{-\frac{k_2}{\Delta\nu^2}}\right) + \ \ldots \tag{5}$$

where $c_0, c_1, c_2, \ldots, c_i$ and $k_0, k_1, k_2, \ldots, k_i$ are the constants to be determined. Such a choice of the solution is suggested by the circumstance that the separate terms of this function have a definite similarity with the function of the distribution of the intensity of the line emitted by the lamp and also, as far as we can judge, some remote likeness to the function of the distribution in the scattered line $I(\Delta\nu)$. As will be seen later, it suffices to take a small number of terms to have function (5) reproducing with sufficient accuracy the real curve of the distribution of intensity within the Rayleigh line.

Such a choice of the solution has yet another advantage; after substituting it into eq. (1), the integration can be easily performed. It only remains to select or determine the quantities $k_i$ and $c_i$ in order to obtain a complete solution.

Let us take for the beginning the solution in the form of a single term $I(\Delta\nu) = \left(1 - e^{-\frac{k}{\Delta\nu^2}}\right)$. In order to facilitate integration, we will consider only such values of the transmittance $A$ for which a practically complete absorption takes place in the centre of the line. Then we must exclude from consideration the initial part of the curve $A(T)$, when absorption is weak. This implies that the structure of the most central part of the line (up to $\pm 0.1 - 0.2$ cm$^{-1}$) will not be considered either.

Under these conditions we always have

$$\Delta\nu^2 > \left(\frac{\gamma}{4\pi}\right)^2, \qquad M \gg \left(\frac{\gamma}{4\pi}\right)^2$$

and formula (3) may be substituted with a simpler one

$$\frac{4\pi n x l}{\lambda} = \frac{M}{\Delta\nu^2}. \tag{3 bis}$$

Now eq. (1) transforms into

$$A = \frac{\int_{-\infty}^{+\infty} \left(1 - e^{-\frac{k}{\Delta\nu^2}}\right) e^{-\frac{M}{\Delta\nu^2}}\, d\nu}{\int_{-\infty}^{+\infty} \left(1 - e^{-\frac{k}{\Delta\nu^2}}\right) d\nu}. \tag{6}$$

By integrating we get

$$A = \frac{\sqrt{k + M} - \sqrt{M}}{\sqrt{k}}. \tag{7}$$

In this simple form, however, this formula is not applicable to our problem. In our experiments we measured the sum of the intensities of two natrium lines $D_1$ and $D_2$. It is easy to allow for the different absorption of these lines by taking the absorption coefficient of the line $D_2$ to be twice that of the line $D_1$. This assertion has been proved by numerous experiments. But to

make allowance for the emission difference of those lines is a more difficult matter. The lines $D_1$ and $D_2$, emitted by the lamp, are of different width and intensity and have also a different value of self-reversibility. The difference in width and self-reversibility has practically no significance, if we do not consider at all the region of the principal line and restrict ourselves to the investigation of the intensity distribution in the Rayleigh line, starting with some short distance from the centre of the line. Then we can consider the shape of both Rayleigh lines $D_1$ and $D_2$ as precisely identical, and these intensities proportional to the intensities of the exciting lines $D_1$ and $D_2$. The ratio of the intensity of the exciting line $D_2$ to that of $D_1$ can be determined experimentally. Let us denote it by $\alpha$. Then analogously to eq. (6) we shall have

$$A = \frac{\int_{-\infty}^{+\infty} \left[ (1 - e^{-\frac{k}{\Delta\nu^2}}) e^{-\frac{M}{\Delta\nu^2}} + \alpha (1 - e^{-\frac{k}{\Delta\nu^2}}) e^{-\frac{2M}{\Delta\nu^2}} \right] d\nu}{\int_{-\infty}^{+\infty} \left[ (1 - e^{-\frac{k}{\Delta\nu^2}}) + \alpha (1 - e^{-\frac{k}{\Delta\nu^2}}) \right] d\nu} \quad (8)$$

Here $M$ and $2M$ determine the absorption of lines $D_1$ and $D_2$, respectively. By integrating we get

$$A = \frac{(\sqrt{k+M} - \sqrt{M}) + \alpha (\sqrt{k+2M} - \sqrt{2M})}{(1+\alpha)\sqrt{k}} \quad (9)$$

If we take solution in a more general form (5), we will have

$$A = \frac{1}{1+\alpha} \cdot \frac{c_0 [(\sqrt{k_0+M} - \sqrt{M}) + \alpha (\sqrt{k_0+2M} - \sqrt{2M})]}{c_0\sqrt{k_0} + c_1\sqrt{k_1} + c_2\sqrt{k_2} + \ldots} +$$

$$+ \frac{c_1 [(\sqrt{k_1+M} - \sqrt{M}) + \alpha (\sqrt{k_1+2M} - \sqrt{2M})] + \ldots}{c_0\sqrt{k_0} + c_1\sqrt{k_1} + c_2\sqrt{k^2} + \ldots} \quad (10)$$

We must point out that the latter formulae do not take into account the additional absorption of the first Rayleigh line $D_1$ in the region of $D_2$ and of the second Rayleigh line $D_2$ in the region of $D_1$. The two absorption lines $D_1$ and $D_2$ are located only at a distance of 6 Å, and therefore each one of the Rayleigh lines $D_1$ and $D_2$, while passing through the absorption tube with natrium, acquires two absorption bands. The second of these bands located asymmetrically at a distance of 6 Å from the centre is not taken into account by our formulae. However, since the intensity in the Rayleigh line decreases comparatively from the centre, this circumstance can be allowed for approximately by a correction.

In the case of a single resonance line it would be easy to get quite an exact idea of the shape of the scattering line if we plot a curve $-\frac{dA}{d\sqrt{M}}$, where $\sqrt{M}$ corresponds to half the width of the absorption region. In our case when we have two lines of emission and two absorption regions of different intensity, the curve $-\frac{dA}{d\sqrt{M}}$ also gives some idea of the shape of the emission line, though a much rougher one.

Before proceeding to the exact calculation, we plot the curve $-\frac{dA}{d\sqrt{M}}$. Basing on this curve, we choose the parameter $k_i$. For our computations we take seven terms in eq. (5). Then we write down eq. (10) for six values

of $M$ and $A$ suitably chosen. We will get a set of six equations for the determination of six unknown parameters $c_1, c_2, \ldots c_6$. We put $c_0$ equal to 1.

$$\left.\begin{aligned}
v_{11}c_1+v_{12}c_2+v_{13}c_3+v_{14}c_4+v_{15}c_5+v_{16}c_6 &= -v_{10}\\
v_{21}c_1+v_{22}c_2+v_{23}c_3+v_{24}c_4+v_{25}c_5+v_{26}c_6 &= -v_{20}\\
v_{31}c_1+v_{32}c_2+v_{33}c_3+v_{34}c_4+v_{35}c_5+v_{36}c_6 &= -v_{30}\\
v_{41}c_1+v_{42}c_2+v_{43}c_3+v_{44}c_4+v_{45}c_5+v_{46}c_6 &= -v_{40}\\
v_{51}c_1+v_{52}c_2+v_{53}c_3+v_{54}c_4+v_{55}c_5+v_{56}c_6 &= -v_{50}\\
v_{61}c_1+v_{62}c_2+v_{63}c_3+v_{64}c_4+v_{65}c_5+v_{66}c_6 &= -v_{60}
\end{aligned}\right\} \qquad (11)$$

$$c_{ik}=(\sqrt{k_k+M_i}-\sqrt{M_i})+\alpha(\sqrt{k_k+2M_i}-\sqrt{2M_i})-(1+\alpha)\,A_i\sqrt{k_k}. \qquad (12)$$

For computing $M$ with the aid of eq. (4), we take the value of $\rho$ from the paper by Ladenburg and Minkovsky (2) and find the damping constant $\gamma$ from the formula

$$\gamma=4\sigma^2 N\sqrt{2\pi kT\frac{m_1+m_2}{m_1\cdot m_2}}\,. \qquad (13)$$

Here $\sigma$ is the optical diameter for the pair $N_a-N_2$ which I take to be equal to $7.7\times10^{-8}$ cm, basing on Minkovsky's (3) measurements. $N$ is the

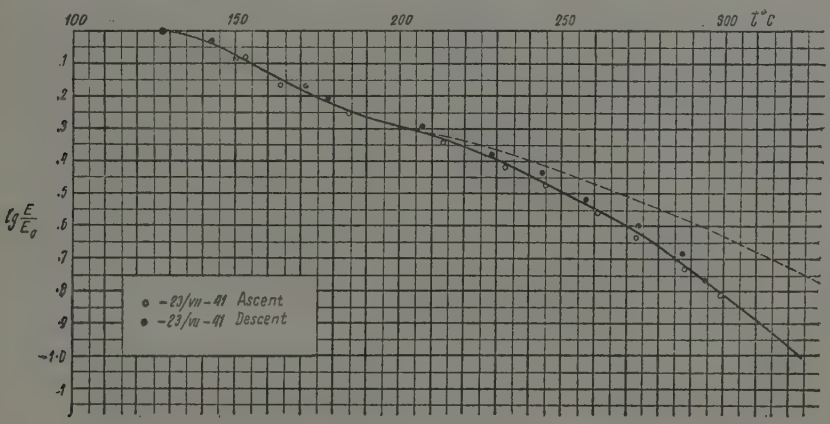


Fig. 1.

number of nitrogen molecules per cm³; $N=p/kT$; $k$, the Boltzmann's constant; $T$, the temperature in absolute scale; $p$, the pressure of nitrogen; $m$, the mass of natrium atom; $m_2$, the mass of a molecule of nitrogen.

The dependence between pressure and temperature for the region we are interested in, is the following:

$$p=47+0.55T. \qquad (14)$$

Substituting into eq. (4) instead of $l$ 43.5 cm and instead of $\gamma$ the corresponding expression depending only upon $T$, we will get an expression for $M$ in $\mathrm{cm}^{-2}$:

$$M=1.51\times10^{-23}\,\frac{47+0.55T}{\sqrt{T}}\,\rho. \qquad (15)$$

The transmission of scattered light from benzene by an absorption tube is shown on Fig. 1. On the abscissa axis $t$ is plotted; on the ordinate axis $\lg A$. The full curve is drawn through experimental points; the dotted curve shows the same after the elimination of additional absorption. The latter curve has served us as a basis for the calculation of the shape of the Rayleigh line.

In Table 1 are given those values of $M$ and $A$ which we have chosen for substitution into formula (12). In the columns next to them we give the corresponding values of $T$ and $\rho_{D_1}$. The comparison of the intensities of the emission lines $D_1$ and $D_2$ under a stationary regime of the lamp showed them to be absolutely identical.

This means that in our formulae we have to put $\alpha = 1$. The parameters $k_i$ were chosen as follows: $k_0 = 0.0625$, $k_1 = 0.25$, $k_2 = 1$, $k_3 = 4$, $k_4 = 16$, $k_5 = 64$, $k_6 = 256$.

Table 1

| $T$ | $\rho_{D1} \cdot 10^{-22}$ | $M$ | $A$ |
|---|---|---|---|
| 430 | 0.02396 | 0.0488 | 0.766 |
| 460 | 0.1511 | 0.319 | 0.555 |
| 490 | 0.7527 | 1.64 | 0.462 |
| 520 | 3.092 | 6.93 | 0.374 |
| 550 | 10.80 | 24.9 | 0.2911 |
| 580 | 32.99 | 78.1 | 0.2163 |

After calculating the values $v_{ik}$ with the aid of eq. (12) and after solving the set of equations (11), the following values of the constants $c_i$ are received: $c_0 = -1$, $c_1 = +1.714$, $c_2 = -0.8361$, $c_3 = +0.2473$, $c_4 = -0.04091$, $c_5 = +0.00625$, $c_6 = +0.00419$. As is seen from Table 2, the curve $A(T)$, built according to the data obtained by using formula (10), agrees perfectly with the experimental curve. Those values of $A$ which are used for calculating the parameters $c_i$ are printed in fat type.

Table 2

Comparison of Experimental and Calculated Values for Scattered Light Transmission by an Absorption Tube

| $T$ | $A$ | | $T$ | $A$ | |
|---|---|---|---|---|---|
| | experimental | calculated with the aid of (10) | | experimental | calculated with the aid of (10) |
| 245 | 0.813 | 0.805 | 490 | **0.462** | 0.462 |
| 430 | **0.766** | 0.766 | 495 | 0.450 | 0.448 |
| 435 | 0.725 | 0.725 | 500 | 0.434 | 0.434 |
| 440 | 0.679 | 0.684 | 510 | 0.405 | 0.404 |
| 445 | 0.646 | 0.646 | 520 | **0.374** | 0.374 |
| 450 | 0.610 | 0.611 | 530 | 0.345 | 0.345 |
| 455 | 0.581 | 0.580 | 540 | 0.316 | 0.317 |
| 460 | **0.555** | 0.555 | 550 | **0.291** | 0.291 |
| 465 | 0.535 | 0.534 | 560 | 0.268 | 0.265 |
| 470 | 0.515 | 0.517 | 570 | 0.242 | 0.240 |
| 475 | 0.501 | 0.502 | 580 | **0.216** | 0.217 |
| 480 | 0.490 | 0.489 | 590 | 0.194 | 0.194 |
| 485 | 0.476 | 0.475 | 600 | 0.174 | 0.172 |

At no point does the calculaced curve $A(T)$ deviate from the experimental one by more than one per cent.

Therefore the intensity distribution within the Rayleigh line may in our case be expressed by the formula

$$I(\Delta\nu) = -(1 - e^{-\frac{0.0625}{\Delta\nu^2}}) + 1.714\,(1 - e^{-\frac{0.25}{\Delta\nu^2}}) - 0.8361\,(1 - e^{-\frac{1}{\Delta\nu^2}}) + \\ + 0.2473\,(1 - e^{-\frac{4}{\Delta\nu^2}}) - 0.04091\,(1 - e^{-\frac{16}{\Delta\nu^2}}) + 0.00625\,(1 - e^{-\frac{64}{\Delta\nu^2}}) + \\ + 0.00419\,(1 - e^{-\frac{256}{\Delta\nu^2}}). \qquad (16)$$

On Fig. 2 this function is represented graphically. In an analogous way several more calculations of the shape of the Rayleigh line were performed, choosing other values of the parameters $k_i$ and different values of $M$ and $A$ corresponding to other temperatures. In all cases the curves thus obtained differed very little from the ones shown above.

The most important peculiarity of the curve is the existence of a maximum at $\Delta\nu = 1.8\ cm^{-1}$. The intensity does not decrease monotonously, as it has been always supposed. The Rayleigh line may be broken up into two regions, sharply separated from each other; the region of the Rayleigh line proper and the region of the wings of the line. The second region begins at $\Delta\nu \approx 1\ cm^{-1}$. The intensity reaches a maximum at $\Delta\nu \approx 2\ cm^{-1}$, after which it decreases monotonously. The decrease of the intensity in the centre of the line is explained by the self-reversal of lines emitted by the natrium lamp.

The very central part of the Rayleigh line about up to $0.5\ cm^{-1}$ is not expressed exactly by our curve. The reasons for this are given above. But approximately the general shape of the line is given correctly for that region as well.

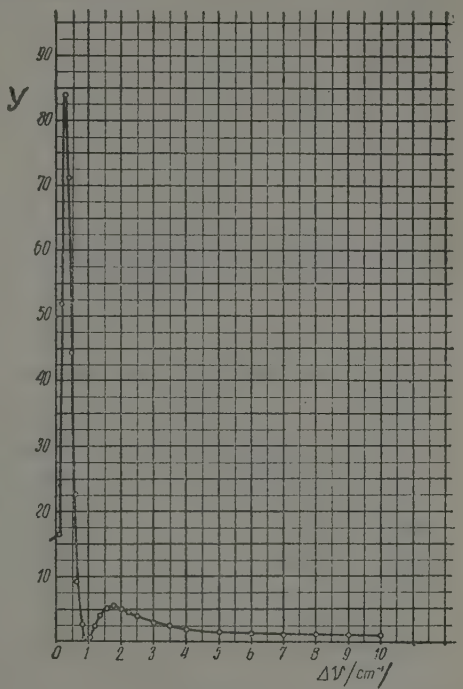

Fig. 2.

The causes responsible for it having this shape will be discussed in a later communication.

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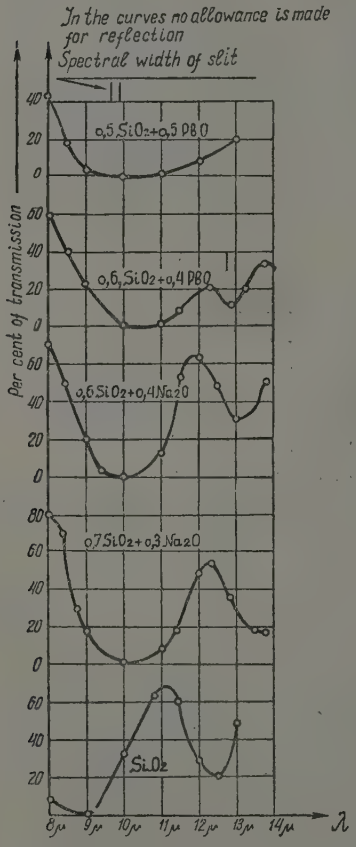
*PHYSICS*

# GLASS STRUCTURE ACCORDING TO INFRARED ABSORPTION SPECTRA

By J. I. GERLOVIN

*(Communicated by S. I. Wawilow, Member of the Academy, 12.X.1942)*

Up to now there is no adequately developed theory of glass structure. The hypotheses so far advanced can be reduced to two fundamental ones. On one of them silicate glasses consist of $SiO_4$ groups, linked together to form a three-dimensional network (1). In contrast with a crystal in the glass there is no periodic arrangement of tetrahedra $SiO_4$; groups that form the network are arranged at random; hence the isotropy of glass. The other hypothesis assumes the presence in the glass of regions with regular arrangement of tetrahedra (2). The experimental data available do not permit as yet to decide the question in favour of either one or the other of these hypotheses. The study of infrared absorption spectra of glass can give additional information on glass structure.




Up to now the infrared absorption spectra of glasses have been investigated using specimens of a thickness of the order of 1 mm. As glasses of this thickness are practically opaque to infrared radiation with a wave-length greater than 5 μ, the region of proper vibrations remained unexplored. To study that region reflection spectra have been used. However, bands of low intensity are obtained by that method with great difficulty and so it must be considered as lacking perfection.

The thickness of the films investigated for absorption by the present author was of the order of 10 μ. At such thickness the glass turned out to be transparent enough to make possible the study of the absorption spectra up to 14 μ for six types of silicate glasses.

From the figure it is seen, that in the spectra of all glasses there is a strong absorption maximum in the region of 9—10 μ. In the absorption spectrum of fused quartz that maximum lies at 9 μ. for other glasses a shift of 1 to 1.3 μ of the absorption maximum towards greater wave-lengths is observed.

In the reflection spectra of fused quartz and other silicate glasses Matossi and Bluschke have found a strong band also at 9 μ.

From calculations the tetrahedron $SiO_4$ appears to have proper vibrations with frequencies corresponding to 9, 12.5, 20.5 and 26 μ; the frequency corresponding to 12.5 μ is inactive.

The appearance in the case of silicate glasses of a band at 9 μ supports the assumption that silicate glasses consist of tetrahedra $SiO_4$. But the fact that this band occurs in the absorption spectrum tells nothing about how these tetrahedra are linked together, regularly or irregularly. The answer to this question may be obtained from studying the absorption spectrum in the region 12—13 μ.

The band at 12.5 μ, corresponding to the inactive proper vibrations of the tetrahedron $SiO_4$, appears, as has been shown by experiment, in the case of crystals with ring-structure. Matossi and Bluschke detected such a band in the reflection spectrum of crystalline and fused quartz and so came to ascribe a ring or crystallite structure to these substances. No such band has been found by them in the case of glasses.

As I have found a band at 12—13 μ in the absorption spectrum not only of fused quartz, but also of other glasses, it follows that in the glass, too, the tetrahedra $SiO_4$ form a ring structure. That fact speaks in favour of the crystallite hypothesis. The absence of this band in the reflection spectrum of glasses is probably due to the fact that the strong band having its maximum at 9 μ overlaps the feeble one lying at about 12 μ; it is because of the overlapping that the feeble band escapes resolution. Now the spectral range of absorption depends on the thickness of the layer. The thickness of the films investigated by us was about 10 μ; at such thickness no overlapping takes place.

With the addition of metal oxides the maxima of absorption bands become more diffuse and are shifted to longer wave-lengths; the heavier the added oxide, the more pronounced are these changes.

Thus it is seen, that the glass has crystalline properties which are gradually fading away as its composition is becoming more complex and the quantity and mass of metal oxides are increased.

In concluding I am glad to express my thanks to prof. M. L. Weingeroff for guidance and valuable suggestions

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*CHEMISTRY*

# ON IRIDIUM SULPHITO-CHLORIDES

By V. V. LEBEDINSKY and M. M. GURIN

*(Communicated by V. G. Chlopin, Member of the Academy, 20.X.1942)*

Besides iridium sulphito-chlorides of the type

$$Me_5[Ir(SO_3)_2Cl_4] \quad (I)$$

and

$$Me_4[Ir(SO_3)_2Cl_3] \quad (II)$$

described in our previous communication (1), the authors succeeded in obtaining sulphito-chlorides also of the type

$$Me_7[Ir(SO_3)_4Cl_2]. \quad (III)$$

The difference in the types of the isolated salts is determined mainly by the regime of the introduction of the sulphito-groups.

In the case of sodium salts the introduction of the sulphito-group within the inner sphere of the chloroiridite proceeds rather easily, and there are formed products of incomplete introduction (2), corresponding to salts of types (I) and (II) (see above).

The process of the introduction of sulphito-groups can be followed up easily by the change in colour of the initial olive-green solution of sodium chloroiridite. When a solution of chloroiridite is mixed with a large excess of sodium bisulphite in the cold, no change in coloration is observed; on the contrary, when the solution is heated, the introduction of the sulphito-group proceeds easily and the solution turns rapidly dark-red. If heating is stopped at this moment, the crystallization of sodium disulphitotetrachloroiridite $Na_5Ir(SO_3)_2Cl_4 \cdot 7H_2O$ takes place almost immediately. In case this salt is isolated in proper time, it can be obtained in a very pure state (1). In the filtrate after its isolation yellow crystals of the sulphito-chloride are formed, the latter containing in the inner sphere four sulphito-groups. According to analysis, in this case a salt is formed, corresponding to the formula $Na_7[Ir(SO_3)_4Cl_2].7H_2O$. Analytical data for this salt are given below.

| | Ir | Na | S | Cl | $H_2O$ |
|---|---|---|---|---|---|
| Calculated, % . . . | 26.23 | 15.62 | 19.26 | 8.75 | 17.12 |
| Found, % . . . . | 26.28 | 15.46 | 19.21 | 8.96 | 16.89 |
| | 26.58 | 16.04 | 19.03 | 8.77 | 16.75 |

The salt is practically insoluble in water and gives up seven molecules of crystallization water at 100°C. Thermally the dry salt is very stable; its decomposition does not take place even at 250° C.

If the separation of the disulphito-salt from the dark-red solution is over and heating is continued, the colour of the solution becomes more feeble and soon turns yellow with a feeble reddish tint. At this moment from the hot (and boiling) solution yellow crystals of the sulphito-chloride begin to separate, having the same formula as the previous salt, but containing five molecules of water.

For $Na_7[Ir(SO_3)_4Cl_2] \cdot 5H_2O$:

| | Ir | Na | S | Cl | $H_2O$ |
|---|---|---|---|---|---|
| Calculated, % | 23.12 | 19.27 | 15.36 | 8.49 | 10.78 |
| Found, % | 23.18 | 18.84 | 15.74 | 8.63 | 10.69 |
| | 23.33 | 19.13 | 15.68 | 9.04 | 10.56 |

This salt differs from the former one and gives up at 100° only four molecules of water, the fifth being given up only at 170°. Thermally this salt is quite stable and its decomposition takes place only after heating above 300°.

It should be noted that both salts, the pentahydrate and the heptahydrate, have probably the same geometrical structure with a cis-position of the inner sphere chlorine atoms. To this points their similar behaviour in response to treatment with ammonium hydroxide [the formation of $Na_3Ir(SO_3)_3(NH_3)_3$], which fact has been discussed in our earlier communication [3].

As the papers by Claus [4], Seubert [5] and Birnbaum [6] pointed out the existence of homogeneous sulphito-salts of iridium of the type $Me_3[Ir(SO_3)_3]$ and $Me_6[Ir(SO_3)_5]$, we made an attempt to obtain similar compounds starting from the sulphito-chloride $Na_7[Ir(SO_3)_4Cl_2] \cdot 5H_2O$ described above by treating it with sulphurous acid. However, the result obtained was quite unexpected. Even a slight heating of the crystals of the initial salt in an aqueous solution of sulphurous acid led to the solution of the salt. The process of dissolution was preceded by change in colour; the yellow colour of the salt rapidly changed to a white one. The solution obtained was heated to 100° and then made somewhat more concentrated by evaporation. After cooling, transparent plates of a silky lustre separated from it. Analysis showed that an acid salt had formed of the composition: $Na_5H_2Ir(SO_3)_4Cl_2 \cdot 10H_2O$.

| | Ir | Na | S | Cl |
|---|---|---|---|---|
| Calculated, % | 21.90 | 13.04 | 14.55 | 8.04 |
| Found, % | 22.08 | 13.10 | 15.02 | 7.70 |
| | 21.81 | 12.87 | 14.97 | 8.18 |

As a result of this experiment it was found out that no further introduction of sulphito-groups had taken place and that merely two sodium ions had been given up by the outer sphere:

$$Na_7[Ir(SO_3)_4Cl_2] + H_2SO_3 \rightarrow Na_5H_2Ir(SO_3)_4Cl_2 + Na_2SO_3.$$

In the formula of the solid salt there are no brackets separating the inner sphere from the outer one. They are omitted intentionally, because the value of the molecular electroconductivity of this salt, which is rather soluble in water, proved, contrary to expectation, to be very low: at $v = 1000$ ml $\mu = 458$; at $v = 2000$ ml $\mu = 498$.

According to Werner and Miolati [7], the values for molecular conductivity correspond approximately to pentaionic electrolysis [generally speaking, Werner and Miolati have fixed no «limits» of electroconductivity for complex salts of this kind, derived from such polybasic hypothetic acids as is, for instance, $H_7Ir(SO_3)_4Cl_2$]. If a complete dissociation of the salt had taken place in the

case examined, an octaionic electrolyte would have been formed. Even making allowance for a reduced mobility of the anion, the total value of electroconductivity is still very much too low. Possibly, in this case two hydrogen atoms are bound in a certain very homeopolar way with the sulphito-residues and are within the inner sphere, being thus «undissociated» hydrogen atoms. In the latter case the formula of the salt should be written as follows:

$$Na_5[Ir(SO_3H)_2(SO_3)_2Cl_2] \cdot 10H_2O.$$

Actually, the solution of this salt shows no acid reaction (lithmus paper does not become red and the solution of phenol-phtalein remains coloured yellow-orange). But even if the last formula is accepted, the «limits» of Werner and Miolati will not be satisfied. An agreement with these «limits» will be achieved only if one sodium atom is referred to the inner sphere, i. e. if the formula $Na_4[Ir(SO_3Na)(SO_3H)_2SO_3Cl_2] \cdot 10H_2O$ is accepted. However, the writers cannot venture to insist upon such a coordination structure of the formula of the salt only in order to «conciliate» the values of electroconductivity observed with the formula of the salt, but have instead the intention to continue these investigations.

The acid salt can be prepared by using other methods as well (2).

Under the action of NaOH the acid salt is converted back into the neutral salt $Na_7Ir(SO_3)_4Cl_2$.

If KOH, NaOH or $NH_4OH$ solutions are poured over the crystals of the white acid salt, the latter soon becomes yellow, which may be taken to mean that the hepto-substituted salt is formed again.

Contrary to this, the action of any very diluted acid on the yellow salt leads, first, to a change of the yellow colour of the crystals into a white one, and only some time later the dissolution of the salt takes place.

We are faced here probably with a reversible reaction of a very general type:

$$Me_2Na_5Ir(SO_3)_4Cl_2 \underset{\text{base}}{\overset{\text{acid}}{\rightleftharpoons}} Na_5H_2Ir(SO_3)_4Cl_2.$$

As a confirmation of this process we obtained yellow crystals of an ammonium-sodium «mixed» salt $Na_5(NH_4)_2Ir(SO_3)_4Cl_2$, for which:

| | Ir | Na | S |
|---|---|---|---|
| Calculated, % . . | 23.91 | 3.47 | 15.88 |
| Found, % . . . . | 24.18 | 3.96 | 16.39 |

Finally, it should be noted that in contrast with the sodium salts described here, for the ammonium and potassium salts no sulphito-chlorides of the I and III types have been obtained. These salts are inclined to yield only sulphito-chlorides of the II type. These compounds will be the subject of the next communication.

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*CHEMISTRY*

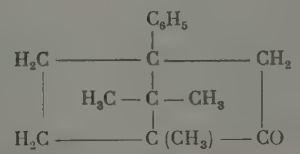
# ON CERTAIN NEW DERIVATIVES OF 4-PHENYL-CAMPHOR

By S. S. NAMETKIN, Member of the Academy, and T. V. SHEREMETEVA

4-phenyl-camphor has been first synthetized by Bredt in 1918 (1), starting from *tert.*-phenyl-borneol, obtained according to Grignard by the action of phenyl-magnesium bromide on camphor, and further through phenyl-camphene and *sec.*-phenyl-isoborneol. However, the position of the phenyl group in this ketone has been determined erroneously. The correct structure of this homologue of camphor was established only in 1929 by S. S. Nametkin, A. S. Kitchkina and D. N. Kursanov (2), these authors having applied in this case a new type of camphene rearrangement, recently discovered in the same laboratory and to which the name of camphene rearrangement of the 2nd type has been given (3). Somewhat later S. S. Nametkin and A. S. Kitchkina have described several new derivatives of 4-phenyl-camphor, in particular *p*-nitro- and *p*-aminophenyl-camphor (4).

In the present paper the number of synthetized derivatives of 4-phenyl-camphor has been considerably enlarged. The description of the newly prepared derivatives of 4-phenyl-camphor is given below, as well as certain new data concerning the preparation and characteristic of previously described compounds belonging to this interesting, but rather inaccessible series of camphor derivatives.

4-Phenyl-camphor



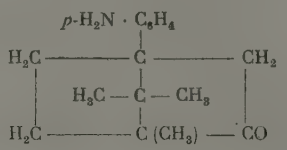

The synthesis of 4-phenyl-camphor has been carried out, in the main, according to the method described previously (2). Only the first two stages of the process have been somewhat simplified as follows. After the reaction of camphor with phenyl-magnesium bromide is over and camphor not having entered the reaction has been distilled off with steam, the residue consists of a ternary mixture: *tert.*-phenyl-bornyl alcohol, the product of its partial dehydration, phenyl-camphene and a side product of this reaction, biphenyl. It proved to be more simple not to separate this mixture into components, but to treat it further, viz. by heating it with potassium bisulphate, to bring to an end the dehydration of the tertiary alcohol and to treat the binary mixture thus obtained, consisting of phenyl-camphene and biphenyl, with acetic acid, according to Bertrand and Walbaum.

The *sec.*-phenyl-isobornyl acetate thus obtained can be easily isolated from its mixture with biphenyl and after crystallization from ethyl alcohol

has the melting point given previously (87°). The yield of the ester based on camphor used in this reaction was never above 7% of the theoretical.

The hydrolysis of *sec.*-phenyl-isobornyl acetate and the conversion of the alcohol obtained into 4-phenyl-camphor was carried out in complete agreement with the method described formerly (2).

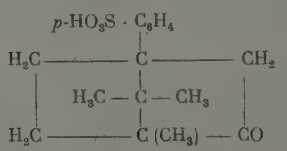
4-*p*-Aminophenyl-camphor



The amine (m. p. 144.5—145°) was obtained in this case as well by the reduction of 4-*p*-nitrophenyl-camphor (m. p. 150—151°) with zinc dust in an acetic acid medium. A new derivative of 4-*p*-aminophenyl camphor, the acetyl one, has been prepared and analysed: a colourless, crystalline substance, m. p. 181—182°.

In addition to the already published observations(4) it has been found out that the amine obtained by reducing nitrophenyl-camphor during a long time, and carefully purified by converting it into its sulphate, crystallized from alcohol, does not show the properties of an indicator of the hydrogen ion. Such properties are peculiar only to an amine that has not been sufficiently purified, owing, probably, to the admixture of an intermediate or by-product of the reduction of 4-*p*-nitrophenyl-camphor. The nature of this interesting indicator has not been quite established as yet.

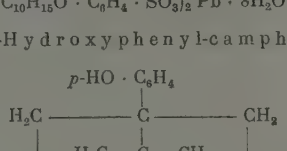
4-*p*-Sulphophenyl-camphor



This sulphonic acid was prepared by the action on 4-phenyl-camphor of 5 parts of sulphuric acid monohydrate under heating on a water bath at 35—40° C. The free sulphonic acid was isolated from the aqueous solution of its lead salt by the action of hydrogen sulphide. After crystallization from chloroform this acid is a colourless crystalline substance, m. p. 189—190°. When crystallization is carried out slowly, small trunkated prisms are obtained. The barium and the lead salts of this sulphonic acid have been prepared and analysed. These salts have the following composition:

$(C_{10}H_{15}O \cdot C_6H_4 \cdot SO_3)_2\,Ba \cdot 6H_2O$ and
$(C_{10}H_{15}O \cdot C_6H_4 \cdot SO_3)_2\,Pb \cdot 8H_2O$.

4-*p*-Hydroxyphenyl-camphor



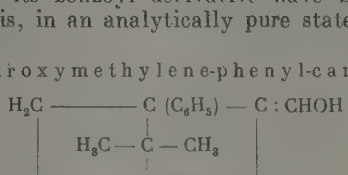
This interesting compound can be given also the name of 4-phenol-camphor. Attempts to prepare it have been made already before (4), but have not been brought to an end. In the present investigation 4-*p*-phenol-camphor has been prepared through the decomposition at room temperature of the aqueous solu-

tion of the diazotized amine, 4-*p*-aminophenyl-camphor. Phenol-camphor separates as a flaky yellow precipitate with the admixture of a resin. The time necessary for the decomposition of 2.5 g of the diazotized amine was 20 days. This new derivative of 4-phenyl-camphor, purified through repeated crystallization from a mixture of gasoline (1 part) with benzene (2 parts), was obtained as fine colourless elongate prisms and clusters, m. p. 125°.

4-*p*-phenyl-camphor was characterized through its benzoyl derivative (according to Schotten-Baumann), that crystallizes from ethyl alcohol in needles and clusters, m. p. 175—176°.

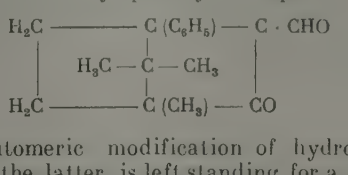
4-*p*-phenyl-camphor and its benzoyl derivative have been obtained by the writers, as shown by analysis, in an analytically pure state.

3.4-Hydroxymethylene-phenyl-camphor



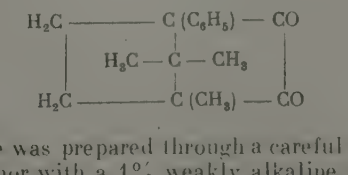
This derivative of 4-phenyl-camphor was prepared, according to Claisen, by the condensation of phenyl-camphor with isoamyl formiate in the presence of sodium. Purified by dissolving it twice in alkali and consequently displacing it with acetic acid, the substance proved to be crystalline, m. p. 50—54°. Its benzoyl derivative, prepared according to Schotten-Baumann, is a colourless crystalline substance, which after crystallization from alcohol has a m. p. 149—150°.

3.4-Formyl-phenyl-camphor



This compound is a tautomeric modification of hydroxymethylene-phenyl-camphor; it is formed when the latter is left standing for a long time in an open vessel at room temperature in an aqueous solution of acetic acid. The gradual evaporation of the solvent leads to a separation of a crystalline substance. After 2 months, when the odour of acetic acid had disappeared, the residue was crystallized from gasoline. The substance had a m. p. 91 —95°. The new substance differed from hydroxymethylene-phenyl-camphor in that it did not yield a benzoyl derivative. When heated with an ammoniacal solution of silver nitrate, metallic silver separated from the solution. All these data make it possible to affirm that under the specified conditions 3.4-hydroxymethylene-phenyl-camphor is converted completely into its tautomeric modification, 3.4-formyl-phenyl-camphor.

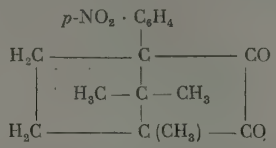
4-Phenyl-camphorquinone



4-phenyl-camphorquinone was prepared through a careful oxidation of 3.4-hydroxymethylene-phenyl-camphor with a 1% weakly alkaline solution of potassium permanganate in the cold. The quinone was extracted from the reaction mixture with ether. After the solvent was distilled off and the residue crystallized from dilute alcohol, the quinone was obtained in an analytically pure state, m. p. 142—143°. Slow crystallization from gasoline yields the substance in large yellow prisms.

Bredt has described briefly this substance and given its melting point as 145°(1).

4-*p*-Nitrophenyl-camphorquinone



This derivative of 4-phenyl-camphor was prepared by the action of selenium oxide on 4-*p*-nitrophenyl-camphor in an acetic anhydride medium, according to the well known method of Asahina and Ihodata. From a cooled solution in glacial acetic acid the quinone precipitated in well formed fine yellow crystals, m. p. 137°.

Slow crystallization from acetone yields large prisms.

## Conclusions

1. The method previously described for the preparation of 4-phenyl-camphor has been somewhat simplified.

2. Some new data have been obtained concerning the synthesis and the characteristic of the previously described derivatives of 4-phenyl-camphor, viz. 4-*p*-aminophenyl-camphor and 4-phenyl-camphorquinone.

3. The following new derivatives of 4-phenyl-camphor have been prepared for the first time and characterized: 4-*p*-sulphophenyl-camphor and its barium and lead salts, 4-*p*-hydroxyphenyl-camphor, 3.4-hydroxymethylene-phenyl-camphor and 3.4-formyl-phenyl-camphor, 4-*p*-nitrophenyl-camphorquinone.

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*GEOLOGY*

# STRATIGRAPHIC POSITION OF MANGANESE ORE FORMATIONS IN SIBERIA

By A. G. VOLOGDIN, Corresponding Member of the Academy

Until lately the question of the origin of manganese occurrences in Siberia could not, possibly, be solved in any but quite an unsatisfactory way because of lack of comparative data on the geology of the respective regions. First of all, for a considerable portion of the profile of ancient deposits in some of these regions, there was wanting any normal stratigraphic basis, while too often attempts had been made to make up this deficiency by considerations of purely speculative character, which could hardly be relied upon. But there was also another very important circumstance that further complicated the situation. Namely, the fact that with regard to several deposits of manganese the question of their genesis had received no adequate treatment. Now, the manganese deposits of Siberia are associated mainly with ancient formations. Therefore in dealing with the problem of their age, one is dependent upon the advance of paleontological knowledge concerning the strata in which they are imbedded and which have been found to belong to the Cambrian. So the problem of stratigraphic interrelations existing between different deposits of manganese ore in Siberia remained intractable until the possibility of solving it was opened by this author, having compiled the available data bearing on Cambrian stratigraphy in USSR into a comprehensive volume which was planned to make a part of a series of monographies on the stratigraphy of the USSR, a work undertaken on the initiative of A. D. Archangelsky, late Member of the Academy.

In Siberia the deposits of manganese are known in the region of the Arga range near the town of Achinsk; in the vicinity of vil. Nikulina, on the western slope of the East Sayans; in the Kusnetsk Alatau, along the river Ussa; and within the extension of the Salairsk ridge, near v. Durnovaya.

Scarcely any signs were ever noticed previously which might permit to tie in these deposits with one another. Their enclosing rocks were referred to different stratigraphic complexes from pre-Cambrian down to Silurian.

The Mazul beds of manganese ores within the mountain range of Arga have long been put upon a wrong interpretation. They have often been represented as metathetic formations on the ground, that these ore accumulations are associated with old karst sink-holes in a stratum of most ancient carbonate rock (sometimes freely referred to pre-Cambrian) and lie in the neighbourhood of well developed metamorphic vulcanogenic rocks. Other investigators, on the basis of more recent data, found it possible to separate from these ores a zone of hydrothermal origin as well as a transition zone to primary carbonate manganese ores associated stratigraphically with a stratum of dark, marble-like limestones which have partly become carbonaceous or turned into silica and quartz. In tectonic contact with these limestones are lying metamorphous green basic rocks which are considered to be the younger formations. These are sandstones, shales and,

partly, limestones. For determining the age of this lithologically complicated set of rocks, no weighty evidence was available formerly. A. A. Vassiliev, the explorer of the Arga range, had provisorily referred the above two groups of metamorphic rocks to the «Upper Algonkian», though he admitted that similar deposits were extensively developed in the Kuznetsk Alatau which is the adjoining massif. The latter has been persistently investigated for many a year by J. S. Edelstein, D. V. Nikitin, O. K. Poletaeva and the author, and the result of their work is that its ancient carbonate deposits are now referred to Lower or Middle Cambrian as they have been found to contain Cambrian trilobites, archeocyates, calcareous algae, etc. in a very great number of places. For Salair and Kuznetsk Alatau the author from his paleontological investigations, made on collected specimens and in the field, was also able to determine the age of their old vulcanogenic complex of rocks which he found essentially to be Middle Cambrian.

It was long before any organic remains were encountered in old carbonate deposits of the Arga range. Only in 1937 did the author come across some algal formations in the region of the mine Mazulka. These were identified as accumulations of a typically Cambrian form (*Epiphyton fasciculatum* Chapm.). The finding of these algae directly in the region of the deposit settles the question as to the age of the old metamorphic limestones enclosing the ore. Another valuable evidence to the same effect was produced in the summer of 1941 by O. K. Poletaeva, who during some supplementary stratigraphic investigations discovered here also remains of archeocyates. The above findings testify to the alliance of the Arga range with the neighbouring massifs—the Kuznetsk Alatau and the range of Krasnoyarsk, the latter being the north-western spur of the East Sayans.

Thus, concerning the age of the primary carbonate manganese ores of the range of Arga, we have now obtained data pointing to the beginning of the Middle Cambrian. It was the time when in the whole region over which the northern and eastern portions of the Kuznetsk Alatau extend at present, the accumulation of thick carbonate sediments in the form of muds and archeocyate reefs had been stopped by the local development of bottom vulcanism, which had radically changed the chemism of the basin and unfavourably affected the development of fauna and flora in some of its parts. Occasional shallowing, thermal conditions peculiar to the sea and the introduction of new chemical elements into the basin appear to have created in the region of the Arga range, at the very beginning of the Middle Cambrian, a geochemical situation encouraging the progress of microbiological processes, in general, and favourable for the development of manganese assimilating bacteria, in particular. Just how great was the area of the manganese-bearing sediments that had been deposited here, and what was their composition and thickness, cannot yet be stated definitely, but it may be surmised that it was no small area. Along with the accumulations of manganese a significant rôle in the region of Arga has been played by the products of the life-activity of iron bacteria, and at times by those due to phosphorus bacteria, and others.

Within the reach of the western slope of the East Sayans the vulcanogenic rocks of the Middle Cambrian are not uniformly developed at all places, which is only natural in view of the vast extent of the area now occupied by this mountainous massif. The manganese ores lying near the vil. Nikulina are secondary formations developed in the area of Cambrian limestones and old green rocks. Field investigations made by the author within 1924—1928, in which he disclosed the presence of archeocyate fauna in crystalline limestones, permit to look upon the formation of manganese ores here as again connected with the biochemical phenomena that took place on the boundary between the Lower and Middle Cambrian. Unfortunately, this secondary ore formation being on a small scale, no attention to it was payed by the geologists that surveyed the region, and up to the present the centres of ore formation have not been laid open by working. Therefore our knowledge, concerning the details of the formation of manganese ores in the region of the vil. Nikulina, has made no progress. Yet, on the basis of the legitimate comparison with the paleontological, lithological and strati-

graphic data available from other districts, e. g. from the range of Arga, one may expect to find that the primary development of manganese ore is here on a broader scale than it would appear from the outcrops of secondary ores at vil. Nikulina.

In 1939 a reconnoitering party of the West Siberia Geological Administration including several workers of the West Siberia Gold-Prospecting Trust discovered a new deposit of manganese (Ivanovskoe) on the river Ussa, in the basin of riv. Tom. This at once was given close attention on the part of geologists and surveyers. owing to indications for the presence of big stores of manganese here. Very optimistic assumptions were made as to the practical value of this deposit (K. V. Raduguin). In the summer of 1939 the basin of the riv. Ussa was brought into the field of geological investigation undertaken by A. L. Dodin who studied the stratigraphy and tectonics of that region. He found that the primary ores, not very high in manganese, are associated stratigraphically with the Cambrian. Near and within the ore-bearing zone he discovered a fauna of archeocyates, which permitted to identify the age of the rocks as the lowermost part of Middle Cambrian. The manganese-bearing horizon is lying here amidst thick carbonate Cambrian formations which are folded into a large anticlinal structure of meridional attitude. In the autumn of 1940 Dodin brought to Leningrad new specimens of archeocyates which he had collected for the sake of determination and which proved to belong to two different horizons located at the bottom of the Middle Cambrian. They were, moreover, indicative of the age of the manganese ores lying in the southern portion of the Kuznetsk Alatau, within the basin of the river Ussa.

Similar ideas about the nature of manganese ores arise from the investigation of the north-western part of the Salair range (the Durnovsk deposit). But here only secondary ores of hydrothermal origin have so far been encountered. They are developed in the distribution field of carbonate and vulcanogenic rocks of the Cambrian. Primary ores have not yet been disclosed here, and their special development within the thickness of Cambrian formations is only a conjecture.

From this brief survey of factual data on the development of manganese deposits in Siberia it is quite clear that at one time or several times, during the geological development of that territory, manganese-iron and iron-manganese, occasionally phosphorous, sediments were deposited in sea basins over areas of different extension. This took place at the beginning of the Middle Cambrian and seems to be connected with simultaneous tectonic movements of the lithosphere and with the outset of marine vulcanism which was very intensive in Middle and West Siberia.

It is of considerable interest, from practical as well as theoretical standpoint, that analogous geological materials are known from Kazakhstan. The deposits of phosphorites which have won themselves a wide fame at present, are, according to the recent data on trilobites from the zone overlying the phosphorite zone in the Middle Cambrian profile (E. V. Lermontova), associated stratigraphically with the lower parts of that section also. The fact that a series of phosphorite-bearing layers has appeared in the Kara-tau region, having conglomerates at its basis and including layers of dolomites, sandstones, tuffs, siliceous rocks, glauconite sandstones, etc., must be tied in with special facies of the beginning of Middle Cambrian, which come out to be almost identical stratigraphically with the manganese-bearing sediments of the above-mentioned regions of Siberia. In phosphorite-bearing layers of the Kara-tau, which beside phosphorites contain carbonates, chalcedony, quartz grains, pyrites, glauconite and some organic admixtures, there have been found remains of *Radiolaria* and spicules of sponges. The composition of the rocks points definitely to the facies of estuaria, to the shallowness of the basin and its nearness to the region of the uplift which furnished the clastic material. Some investigators connect the precipitation of phosphates from sea-water with their being deposited as crystals in the apatite lattice, for instance, in the form of hydroxyl apatite, fluorine apatite or isomorphous mixtures. This implies an increased concentration of salts

in the water and a temperature of about 25°C, which two circumstances are in good accord with what we know about the climate of Siberia during the Cambrian. It will suffice to recall the huge accumulation of marine salts in the region of the Siberian table-land at the bottom of Middle Cambrian or, at some places, deeper down below.

According to my data, the effect of the climate which in the case of Kazakhstan and Siberia was a warm, at certain points a hot one during the Cambrian period, was to intensify the biochemical processes involved in the formation of phosphorite deposits. And it has been made perfectly clear by the works of W. I. Vernadsky and A. P. Vinogradov that these processes make for a much greater concentration of salts in the deposits than in the waters of the respective basin. In the warm seas of the territory, now made up by Siberia and Kazakhstan, the deposition of minerals during the Cambrian period, especially at the boundary between Lower and Middle Cambrian and later, was not uniform in all regions, but rather controlled by depth, geotectonic regime and other conditions prevailing in the particular region. Accordingly, different minerals were deposited in different regions. While accumulations of marine salts, for instance, are characteristic of table-land, the geosynclinal type is characterized by archeocyate-reef facies, by facies of manganese, iron, or phosphorus-bearing deposits, etc. In so far as iron has of late been established in certain layers of Kazakhstan phosphorite series, and the manganese ores of the mine Mazulka are known to contain phosphorus, there is reason to believe that these facies not only approach each other very closely in age, but have also formed in a similar biogeochemical situation against the background of the relationship existing between the respective fossil basins.

The picture of the distribution of manganese-iron-phosphorite facies, as traced here, is yet a rather schematic representation. A great deal of field and laboratory work has to be done by geologists and geochemists in order to develop it in greater detail. But there is every reason to expect that the starting of research work under the new angle will unveil much of the history of fossil marine basins and disclose further stores of the above-mentioned as well as new sedimentary useful minerals.

For conducting properly the prospecting work in the case of such minerals that, like the ones dealt with here, are governed by stratigraphy, it is necessary to organize a very careful paleontological and stratigraphic investigation of the regions concerned, by securing the assistance of the most competent workers in both field and laboratory research. Every conclusion as well as every guiding principle laid at the basis of the survey should by well-founded and supported by factual data. The necessity of this is evident to one who remembers that the territory of Central and West Siberia has been interpreted geologically in a number of different ways, which in many points do not agree either with one another or sometimes even with the available paleontological material from the Lower Paleozoic period in Siberia. What is further essential for success in prospecting for manganese and other minerals is a special study of the Cambrian fauna of trilobites and archeocyates, and also of calcareous algae, without which it is impossible to decipher the profiles of Lower Cambrian metamorphic deposits in the regions under investigation.

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*MICROBIOLOGY*

# REPRODUCTION OF TOBACCO MOSAIC VIRUS FROM ITS ACYL DERIVATIVES

By P. AGATOV

*(Communicated by L. A. Orbeli, Member of the Academy, 27.XI.1942)*

It has been established (1) that the virus of tobacco mosaic, after acyl groups are introduced into it, retains its infectuousness to plants. Plant's juice, as has been demonstrated by me, is unable to saponify the acyl derivatives of the virus, its enzymic system being not apparently fitted to bring about this process (2).

The question arises, in what form in this case is the acylated protein of the tobacco mosaic virus reproduced in the plant into which it is introduced?

Looking for an answer to this question I, together with V. L. Rischkov and A. M. Vovk, started some experiments in which tobacco plants were inoculated with the invariable protein of the virus and with its acetyl and benzoyl derivatives.

Two months later, preparations of the virus in question were isolated from these plants, according to V. L. Rischkov and E. P. Gromyko. The obtained preparations were treated not merely for acyl groups, which they were found to contain none, but also colorimetrically for arginine, according to Sacagushi; for histidine and tyrosine, according to Pauli; for tyrosine with Millon's reagent and for groups reacting with phenol reagent. All of the obtained data are listed in the table, where the content of the above amino-acids and groups in these preparations is expressed in per cent to the content of the same groups and amino-acids in a preparation obtained from the plants infected with the protein of the virus.

| Preparation from plants inoculated with | Reaction | | | |
|---|---|---|---|---|
| | Sacagushi | Pauli | Folige | Millon |
| Tobacco mosaic virus . . . . . | 100.0 | 100.0 | 100. | ++++ |
| Its acetyl derivative . . . . . | 100.0 | 97.0 | 100.5 | ++++ |
| Its benzoyl derivative . . . . . | 97.8 | 99.4 | 102.0 | ++++ |

From the tabulated data it is seen that identical preparations were obtained from the plants inoculated with the protein of the virus and from those inoculated with its acetyl or benzoyl derivatives.

As has been mentioned above ([2]), the plants of tobacco appear to have no such enzymic system, as would saponify the acyl derivatives of the virus protein.

The conclusion to be drawn from the data reported here is that an acylated molecule needs no preliminary saponification for reproduction, though what is reproduced is not its own kind of substance (not an acyl derivative), but rather a substance identical with the invariable protein of the tobacco mosaic virus.

The slight modification of the virus molecule due to those chemical groups which do not appear to take any part in reproduction, has no influence upon the formation process or form of the new active virulent substance.

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*BOTANY*

# NATURAL STORE OF WATER IN THE SOIL OF SCRUB DESERTS OF CENTRAL ASIA AS RELATED TO THE PROBLEM OF THEIR RESTORATION

By E. N. BLAGOVESHCHENSKY

*(Communicated by B. A. Keller, Member of the Academy, 17.VI.1942)*

Considerable areas of world's deserts may be described as scrub deserts, for the main components of their vegetation cover are xerophilous shrubs. Such are the mallee-scrubs of Australia, the *Ractama ractem* overgrown tracts of North Africa and the brushes of *Corellea tridentata* and *Prosopis juliflora* in North America. In this group belong also the *Haloxylon* covered deserts of Central Asia.

Though xerophilous, the *Haloxylon* shrubs consume large amounts of water during their growing period, which lasts throughout summer. All of this water cannot possibly be derived from precipitation, because the total of precipitated water is here not very great. Special investigations of the water regime in the soil of the Kara-kum desert, carried on from 1937 till 1942 at Repetek, have shown that even in sandy grounds and when the distribution of precipitation is favourable for the preservation of moisture (85% of it fall within the summer and spring period) the depth of penetration is never above 150 cm and is usually only 60—70 cm. By June the wetted horizon is utterly dry. Now the root system of a *Haloxylon* kind of desert shrub is mainly 3—5 m deep under surface (6) and, accordingly, must be supposed to take up its water from some other source.

The previously advanced assumption that *Haloxylon persicum* and *Haloxylon aphyllum* may obtain the water they need at the expense of ground waters, should now be dropped, for scarcely anywhere across the whole extent of these shrubby deserts do ground waters lie within the reach of *Haloxylon*'s roots, while they are often separated from them by a 10 to 20 m thickness of thoroughly dry sand. At present it may be stated with certainty that the water supporting the life of the shrubs is contained in the «hanging» slightly humid horizons (1.1 to 1.3% humidity) that are formed in certain seasons of the year at a depth of 2 to 5 m*. This appears to be true of the American desert shrub *Schantra* Zon, as well(9). The analysis of temperature and humidity conditions prevailing in the covering and underlying horizons has revealed that moisture is forced to come here from other horisons and is in a state of condensation. Therefore the name of «condensation foci», suggested by B. P. Orlov for these humid horizons, is quite an appropriate term.

* Usually these «hanging» horizons are all the year round separated from the moisture of precipitation and from ground waters by a layer of perfectly dry sand (humidity<0.8%) measuring many meters in thickness.

In the typical case three such foci, the spring, the summer and the winter one, may be distinguished in the yearly cycle. Of them the first is formed by the downward travelling of the precipitation moisture; the second is due to the absorption of water vapour from the atmosphere by the overdried surface of the soil; and the third arises from the sublimation of moisture of ground waters.

The presence of a summer focus of condensation in the sands of Repetek was at some time past observed by Orlov [5], but his data were later refuted by several investigators [3,7]. My observations and experiments have substantially confirmed the views expressed by Orlov except for the statement that condensation largely takes place in the drifting sandy hills known by the local name of «barkhany», because here, according to Orlov, there is no fine grained soil to choke the pores of the ground. I have found that condensation is most intensive just in the lowest elements of the relief, in the so-called «Black *Haloxylon* glens».

In order to make here apparent the condensation horizon, usually absent on account of desuction, it suffices to eliminate the absorption of water from the soil by the roots of the shrubs. At still summer nights a sharply expressed microinversion is observed in the desert, the cold air flowing down from the ridges into depressions where its layer adjoining the surface turns out to be the most saturated with water vapour. The sand dried out in the day-time to a humidity of 0.05—0.1% becomes saturated with hygroscopic water during the night, so that its humidity toward the morning amounts to 0.2—0.3%. By day, owing to the heating of the surface horizons of the soil, the absorbed moisture moves downward and is condensed in the lower horizons, where there is still a certain reserve of winter cold (these are 1 m deep under the surface at the beginning of summer, and 3 m deep at the end) *. Further, it is only natural to suppose that the intensity of the above focus will be comparatively higher in the regions with wider range of temperature. In fact, the area of scrub deserts seems to be marked out by definite temperature boundaries. Thus, on the north the boundary of the *Haloxylon* growth coincides rather closely with a yearly isotherm of temperature equal to 11° at a depth of 3 m below the surface. This is apparently due to the fact that the absolute amount of moisture in the air of the soil is largely a function of temperature. The southern boundary fits in with the isoline running through the points with a yearly air temperature amplitude of 30° C (which corresponds to an absolute yearly range of temperature somewhat higher 100° C). It is just the values of the daily amplitude of temperature throughout the year and during the summer that should determine the intensity of the condensation process, for no sufficient amount of cold can be stored at the lower boundary of the active thermal layer of the soil unless winter cooling is strong enough.

It will be also apparent from what has been stated above that the value of daily amplitudes directly controls the intensity of the process of «molecular» condensation in summer.

South of the 30° isoline the deep-rooted shrubs of *Haloxylon* are replaced by *Salsola arbuscula*, a thinly growing bush with a superficial root system. Still further south the scrubby growth disappears altogether and is superceded by a very rich cover of ephemeral grasses **.

Nature, however, also holds a variety of local factors that affect the position of the boundary between the shrubby and the ephemeral zone in the desert. These may neutralize or else enhance the action of the climate. Prominent among these factors is the depth and mineralization of ground

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* It has been proved by special experiments, in which the water vapour evaporating directly from the soil was collected, that when in the summer time at Repetek the upper layer of sand, 20 cm thick, gives up its water on drying, the main bulk of it (up to 80%) does not evaporate into the atmosphere, but rather migrates to deeper horizons of the ground.

** Described by A. V. Prozorovsky [8] as the «zone of heat exposed meadows».

waters. On the southern boundary of the shrubby desert zone the processes of condensation take place exclusively in the low elements of the relief. This is partly owing to the inflow of cold air and also because of an intensive sublimation of moisture from ground water. In the case of a water table lying lower than 35 m, continuous observations of ground humidity carried on at Repetek from year to year have shown that the sand remained very dry (humidity $<0.8\%$) down to a depth of 8 m (and probably even down to 30 m), except for the horizon wetted through by winter and spring precipitation, which extended from the surface to a depth of 60—90 cm. A sharp decrease in the store of condensation water is also observed when the ground waters are highly mineralized (>5 g per litre), and when chlorides predominate of sulphates, that is when there is $CaCl_2$ in solution.

It has been found out by special experiments that the higher the hygroscopicity of the salts thrown down at the upper limit of the capillary rise, the less the total amount of moisture evaporating from ground waters. The combined effect of the above-mentioned factors is that *Haloxylon* shrubs are not encountered on any of the sandy massifs of Central Asia, situated at the foot of mountain ranges (²), because they have somewhat narrower amplitudes temperature, a deep lying water table and a peculiar stratigraphic composition. In the lowlands of Kara-kum and Kyzyl-kum, areas with saline ground waters are usually occupied by the «white shrub», *Haloxylon persicum*, which is more xerophilous and stunted. And it is only in those regions of the desert in which fresh ground water is available at no greater depth than 20 m, that the «black shrub», or *Haloxylon aphyllum*, can grow and bear fruit with sufficient productivity; for these are the regions with the highest amount of moisture in the root inhabited horizons.

It is a matter of common knowledge that the success of the forest cultivation and meadow reclamation work in the desert depends ultimately upon the conditions of soil wetting, and accordingly, the regions high in moisture are the ones chosen for cultivation. However, the available soil maps of desert territories take no account of the fundamental economical index characterizing a desert soil, viz., its natural store of water. They are useless, therefore, for the purpose of restoring *Haloxylon* brushwoods which present the main fuel basis in the republics of Central Asia.

Thus, we find in them united under the same description of «dusty-sand grey-soils», the soils of the low-lying Kara-kums, which are suitable for the growth of *Haloxylon*, and the soils of the Kara-kum foot-hills, in which the deep horizons are entirely destitute of available moisture.

In the adjoined table based on stationary observations and on those made by different expeditions within a period of five years, the soils of the southern deserts of the USSR are subdivided according to their natural provision with water *.

| Soil variety | Vegetation | Amount of water in July beyond the dead store for a 5 m deep layer, in mm |
|---|---|---|
| Dusty-sand grey-soils (often slightly alkaline under the shrub growth) | | |
| Strongly humid | Black shrub (*Haloxylon aphyllum*) . . . . . | 50 |
| Moderately humid | Mixed shrubs of *Haloxylon* . . | 50—25 |
| Weakly humid | White shrub (*Haloxylon persicum*) . . . . . | 25—10 |
| Nearly dry | *Salsola arbuscula* . . . . . | 10— 5 |
| Dry | Ephemeral grasses . . . . . | <5 |

* It should be noted that their store is replenished every year.

In my reconnoiterig work I made extensive use of the determination of humidity in a 5 to 7 m deep layer of ground [the method of drilling has been described by me in an earlier paper (1)], and I found that the reason why the repeated attempts at the restoration of *Haloxylon* brushwoods in Tadjik Soviet Socialist Republic, counting a period of many years, should be so unsuccessful, lies in the fact that the areas selected for cultivation were insufficiently provided with water.

On the other hand, many hundred hectares in the sand-hill belt of Amu-Daria are believed to be unfitted for the cultivation of *Haloxylon* on the only ground that it is not encountered there, which may well be due to its intensive exploitation that continued for centuries. My investigation of the natural water store of sands carried out in the years 1936—1938 has made it clear that these areas are provided with sufficient amounts of soil moisture to support the growth of very productive large-stem shrubs of *Haloxylon aphyllum*.

This was later confirmed by numerous experiments of their commercial cultivation.

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*EXPERIMENTAL BIOLOGY*

# PHYTONCIDES AND THEIR BACTERICIDAL PROPERTIES

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The name of «phytoncides» was given by B. Tokin to the volatile substances he had discovered. These substances whose chemical nature is still uncertain are emitted by plants in the course of their life-activity and are endowed with bacterio- and protistocidal properties.

The present author found in collaboration with Dr. A. Tebjakina (1932)([1]) that phytoncides of *Allium cepa* L. and *Allium sativum* L. are apt to kill *Bacillus coli*, *B. proteus*, *B. typhi abd.* and *B. staphylococcus*. Even at that state of investigation the discovery of the new bactericides of vegetable origin appeared promising from the standpoint of practical medicine. In so far as Tokin's discovery was of purely biological interest, too, the present author applied himself during several years to thoroughly investigate the bactericidal properties of phytoncides. This note contains a part of the experimental data secured by him.

Out of more than 150 vegetable species investigated by Tokin and his co-workers I dealt largely with onion and garlic.

In the first line, I tested the effect of *Allium cepa* L. upon *B. staphylococcus* and *B. sarcina*. The technique of the experiments was the following. Two drops of a milliard suspension of *Staphylococcus albus* were put on the bottom of a Petri dish; they were added with 10—15 drops of juice freshly squeezed out from an onion, and covered with agar-agar. An experimental culture prepared in this way was placed into a thermostat at a temperature of 36—38° and observed daily. As a control served a similar culture without addition of onion juice. Similar experiments were carried out also with *B. sarcina*.

Out of the 29 tests with staphylococcus 27 gave positive results: in a number of cases the experimental culture showed but a poor growth as compared to the opulent growth in the control, occasionally there was total sterility.

Out of the 10 experiments with sarcina 6 gave the result that should have been anticipated.

Subsequent experiments were run with the purpose to make clear whether the phytoncides have a sterilizing effect upon staphylococci and sarcina, when applied as vapour.

Two drops of a milliard suspension of bacteria were put on the bottom of a Petri dish, added with agar-agar, after which the dish was closed. There was taken another Petri dish with some freshly mashed onion on the bottom. The bacterial culture prepared in the first dish was treated with phytoncide vapour during ten minutes. With this aim in view the former was placed with the bottom upwards over the latter dish containing the onion paste. As control served an identical growth which had not been subjected to a treatment with phytoncides.

The same bacteria were also tested for the effect of garlic phytoncides, the procedure being essentially the same.

Along with experiments of this kind there were also arranged tests with allyl-mustard oil and water extract of *Pinus pumila*. In the first set, a small amount of table mustard was stirred in some warm water. The experiments showed these substances to possess an exceedingly high bactericidal effect, too. In agreement with the statement advanced by B. Tokin, however, I am not inclined to identify the chemical nature of the phytoncides with that of essential oils of plants.

The results of the experiments are summarized in Table 1.

Table 1

Effect of Phytoncides upon Staphyllococci

| Treatment with juice | | | Treatment with vapour | | |
|---|---|---|---|---|---|
| Plant | Number of tests | % of cases with positive results | Plant | Number of tests | % of cases with positive results |
| *Allium cepa* . . . | 29 | 93 | *Allium cepa* . . . | 40 | 60 |
| *Allium sativum* . | 8 | 100 | *Allium sativum* . | 11 | 55 |
| *Pinus pumila* . . | 17 | 94 | Mustard . . . . | 20 | 70 |

Effect of Phytoncides upon *B. sarcina*

| Treatment with juice | | | Treatment with vapour | | |
|---|---|---|---|---|---|
| Plant | Number of tests | % of cases with positive results | Plant | Number of tests | % of cases with positive results |
| *Allium cepa* . . . | 10 | 60 | *Allium sativum* . | 11 | 73 |
| *Allium sativum* . | 5 | 100 | | | |
| *Pinus pumila* . . | 9 | 100 | Mustard . . . . . | 21 | 71 |

The question arises, whether the phytoncides act upon the nutrient medium making it unfit for bacterial growth, or whether their effect is a direct one upon the bacteria?

Experiments arranged with the purpose to settle this point have shown that they affect bacteria directly.

Experiments carried out by other authors go to confirm the results obtained by us.

Particularly illustrative is the picture obtained by Tokin and Neliubova in their experiments on the effect of phytoncides upon *Bacillus tuberculosis* of strain BCG, since the method applied in that case was a 6-minute direct treatment of the bacteria with phytoncide vapour, previous to sowing them in the nutrient medium.

Not all our experiments offered a picture of complete sterility, after the bacterial culture had been subjected to phytoncide treatment; as a matter of fact, the results were rather variegated.

There were cases when the ultimate results of growth proved identical both for the experimental and control culture.

It is no difficult matter to explain this circumstance.

Let us suppose that not all the bacteria, but only part of them have been killed by the action of the phytoncides. If the conditions happen to be favourable for the growth of bacteria, the experimental culture may overreach the control culture, if the latter is in the process of depression.

In such cases the experimentalist is bound to investigate the dynamics of growth of a given culture.

The following circumstance should also be taken into account.

First, as a general rule, the phytoncides produce a powerful sterilizing effect only at the moment they are emitted. Sure enough, because of the technical procedure of the experiments, the bacteria could not always be acted upon with the vapour emitted by the phytoncides immediately, and this is why the effect obtained may vary from experiment to experiment.

The second cause is a no less important.

Our numerous observations have shown that phytoncides of one and the same plant vary essentially as to their sterilizing power, according to the part of the plant from which they are obtained. Thus, those produced from the bottom of the bulb are more efficient than those from other parts. It should be taken into consideration, moreover, that onions which were preserved for a long period of time, are less suitable for our purpose. Consequently, experiments that lasted throughout autumn, winter and early spring could not but yield somewhat varying results.

Let us dwell, in conclusion, on a set of experiments which seem to us to be the most illustrative and of some practical interest, too. I have started some tests with the aim to find out the effect of phytoncides upon the bacterial flora of the oral cavity (the experiments were continued by E. Krasnopevzeva). The technique was a quite simple one.

When investigated *in vitro*, some mucus is taken off from the oral cavity with the aid of a sterile sponge or a platinum loop; the mucus collected is seeded in a Petri dish in an agar-agar medium. The experimental dishes are at once treated with the vapour emitted by phytoncides of a certain plant (gruel prepared from the bottom of an onion, garlic, etc.). For this purpose a dish contaning the bacterial culture to be tested was kept bottom upward during 3—10 minutes over another dish, containing a freshly prepared vegetable mass. As a control served dishes with cultures that had not been subjected to phytoncide treatment. Both kinds of dishes were next put into a thermostat at a temperature of 36—38° C. The colonies were kept under daily observation, allowance being made for the dynamics of growth.

Table 2

Bacterial Flora of Mouth Cavity as Affected by Phytoncides

| Plant | Number of tests | Exposure, in min. | Number of cases with results | | | |
|---|---|---|---|---|---|---|
| | | | Total sterility | Delayed growth | Similar growth of exper. and control | Negative |
| *Allium cepa* | 20 | 3 | 15 | 1 | 3 | 1 |
| » » | 20 | 5 | 15 | 5 | — | — |
| » » | 10 | 10 | 5 | 3 | 2 | 1 |
| *Allium sativum* | 10 | 3 | 9 | — | 1 | — |
| » » | 10 | 5 | 8 | — | 1 | 1 |
| » » | 5 | 1 | 5 | — | — | — |
| *Capsicum* | 5 | 3 | 3 | 2 | — | — |
| » | 5 | 5 | 2 | — | 2 | 1 |
| » | 5 | 10 | 1 | — | 4 | — |
| *Pinus pumila* | 10 | 1 | 9 | 1 | — | — |
| » » | 10 | 3 | 8 | 2 | — | — |
| » » | 5 | 5 | 3 | 1 | 1 | — |
| » » | 5 | 10 | 2 | 2 | 1 | — |
| Total | 120 | — | 85 | 17 | 15 | 3 |

Percentage of positive results—71.

In another experimental set there was also practised seeding of mucus taken from the oral cavity. The patient was next given to chew some onion or garlic during 1—10 minutes. After this mucus is taken off again and seeded in an identical medium and under identical conditions. It was found that in some cases even one minute of chewing garlic proved sufficient to sterilize the oral cavity completely, while the controls displayed the opulent bacterial growth well known to microbiologists.

The above-said is well illustrated by Table 2, summarizing the results obtained by E. Krasnopevzeva.

Thus, the exceptional bactericidal power of phytoncides leaves no room for doubt anymore.

There still remain, however, many obscure points pertaining to the mechanism of action of phytoncides upon the bacteria and to the possibility of applying to medical practice the data obtained by us and by Tokin's co-workers. Part of these questions, however, lie beyond the author's competence.

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